The Grafting and Chemical Modification of Epoxidized Natural Rubber

By

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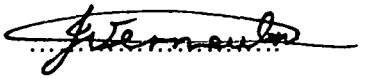
DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.



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ABSTRACT

This study concerns the grafting and chemical modification of a commercially available epoxidized natural rubber (ENR50) by means of the emulsion polymerization technique.

The following were investigated experimentally: three different techniques used for the emulsion polymerization process (batch, delayed addition of monomer and the pre-emulsion polymerization method), the influence of surfactant on the emulsion polymerization reaction, the compatibility of polymethyl methacrylate (PMMA) and polystyrene (PS) with the ENR50, the effect of acrylic and methacrylic acid on the compatibility of ENR50 and PMMA.

A Dynamic Mechanical Analyzer (DMA) and Dielectric Analyzer (DEA) were used, simultaneously, for the analysis of the grafted ENR50 and the DMA was also used separately to evaluate the impact strength of the grafted material.

Using the results of the investigations a series of grafted materials was synthesized in which different surfactant and ENR50 : MMA ratios were used.

This study shows, conclusively, that the best grafting takes place in the reaction using the pre-emulsion polymerization method of MMA with ENR50 and that the simultaneous use of the DMA and DEA can be used as an analytical tool to fine-tune reaction conditions.

OPSOMMING

Die studie het betrekking op die enting en die chemiese modifikasie van 'n kommersiëel beskikbare geëpoksideerde natuurlike rubber (ENR50) deur middel van die emulsie polimerisasie tegniek.

Die volgende is eksperimenteel ondersoek: drie verskillende tegnieke vir die emulsie polimerisasie proses (produksie, stelselmatige byvoeging van monomeer en die pre-emulsie polimerisasie metode), die invloed van seep op die emulsie polimerisasie reaksie, die verenigbaarheid van polimetiel-metakrilaat (PMMA) en polistireen (PS) met die ENR50, die effek van akrielsuur en metakrielsuur op die verenigbaarheid van ENR50 en PMMA.

'n Dinamiese Meganiese Analiseerder (DMA) en Diëlektrikum Analiseerder (DEA) is gelyktydig gebruik vir die analise van die geënte ENR50 terwyl die DMA ook apart gebruik is om die impak-krag van die geënte materiaal te evalueer.

Die resultate van die ondersoeke is gebruik om 'n reeks geënte materiaal te sintetiseer waarin verskillende seep en ENR50 : MMA verhoudings gebruik is.

Die studie bewys, onweerlegbaar, dat enting verkieslik tydens die reaksie plaasvind waar die pre-emulsie polimerisasie metode van MMA met ENR50 toegepas is en dat die gelyktydige gebruik van die DMA en DEA gebruik kan word as die analitiese instrument om die reaksie kondisies fyn in te stel.

The Grafting and Chemical Modification of Epoxidized Natural Rubber

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LIST OF ABBREVIATIONS

T	Absolute temperature
AA	Acrylic acid
ABS	Acrylonitrile-butadiene-styrene
BOTM	Based on the monomer
ΔH	Change in enthalpy
ΔS	Change in entropy
CMC	Critical micelle concentration
°	Degrees
°C	Degrees Celsius
DEA	Dielectric analysis
ε"	Dielectric loss factor
DDI	Distilled deionized water
DMA	Dynamic mechanical analysis
A/D	Electrode area / distance between the electrode
ENR	Epoxidized natural rubber
NP	Ethoxylated nonyl phenol
E.O.	Ethylene oxide
GPC	Gas permeation chromatography
ΔG	Gibbs free energy
T_g	Glass transition temperature
GPEC	Gradient polymer elution chromatography
g	Gram
Hz	Hertz
HIPS	High impact polystyrene
HLB	Hydrophilic / lipophilic balance
LCCC	Liquid chromatography under critical conditions
E"	Loss modulus
LOVA	Low vulnerability ammunition
MAA	Methacrylic acid
MMA	Methyl methacrylate
μm	Micrometer
mN	Millinewton
nm	Nanometer
NR	Natural rubber

NMR	Nuclear magnetic resonance
δ	Phase lag
PMMA	Polymerized MMA (polymethyl methacrylate)
PS	Polystyrene
PVC	Polyvinylchloride
KPS	Potassium persulphate
ε'	Relative permittivity
RT	Room temperature
E'	Storage modulus
TPE	Thermoplastic elastomer
ν	Volume fraction
wt	Weight

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CHAPTER 1

INTRODUCTION AND OBJECTIVES

1.1 INTRODUCTION

Research was done to create a thermoplastic elastomer (TPE) binder that would have the same, or improved, properties as those used in Low Vulnerability Ammunition (LOVA) propellants. LOVA propellants [1] have been made that show excellent resistance to thermal threats [2] such as cook-off and spall attack. Resistance to hypervelocity impact has proven a bit more difficult to overcome. These required properties must, however, not hinder the propellant's ability to meet the energy requirements necessary to attain the established projectile velocity. LOVA propellant composition consists of a finely ground nitramine (RDX) dispersed in a relatively inert binder. Such a binder can be very challenging to formulate since it must possess two basically conflicting properties. Firstly, it must have the ability to absorb localized heat and, secondly it should be able to enhance the energy of the RDX by releasing oxygen [3]. The physical and thermal properties of the binder must also be suitable for proper mixing and processing of the propellant [3]. Suitable binders would therefore be thermoplastic elastomers, which will soften adequately when heated for thorough mixing with the RDX, but will still maintain their toughness and rigidity in the propellant when cooled to ambient temperature.

Epoxidized Natural Rubber (ENR) was therefore used in conjunction with methyl methacrylate (MMA) to create this thermoplastic binder. ENR imparts a low glass transition temperature (T_g) and good impact resistance [4], which will resist fracture by hypervelocity impact, whereas methyl methacrylate contributes to a high T_g. Unique properties of ENR are the epoxide rings that act as a source of oxygen and steric ring strain that enhances energy. The thermoplastic binder was created by the polymerization and grafting of MMA onto ENR. The grafting sites were created on the ENR by the reaction of acrylic/methacrylic acid with the epoxide groups of ENR. The amount of acrylic/methacrylic acid used was controlled to obtain a narrow molecular weight distribution of polymerized MMA (PMMA).

1.2 THE LOW VULNERABILITY AMMUNITION PROGRAM (LOVA)

The low vulnerability program (LOVA) was created by the defence industry to address the problem of the unintentional ignition in conventional propellants (sympathetic detonation) [2]. Such a threat can come in the form of the detonation of a neighboring warhead, fragment impact and direct shaped charge jet impact. S. T. Peters and colleagues, at the naval ordnance station in Indian Head, Maryland, USA, hypothesized that the high order reactions to such threats are the result of the shattering of the propellant grains under the shock of the incident wave. When the large surface area thus generated starts burning, as a result of the hot gases following the detonation wave passing, a violent reaction results.

The inherent relationship between a propellant binder's decomposition temperature and the vulnerability of its respective propellant has been demonstrated in extensive experimental studies [3]. In general, propellants formulated with binders that decompose endothermically are less sensitive than propellants formulated with binders that decompose exothermically, provided that these decomposition temperatures are not significantly higher than those of the energetic components. Also, those binders with the lower endothermic decomposition temperatures are less sensitive than those with endotherms at higher temperatures. This endotherm in the thermoplastic gives the propellant the ability to absorb localized heat from hot fragments before the energetic materials can start to react significantly. However, since it is inevitable that a small quantity of the RDX will decompose on contact with a hot spall, these TPE samples should be tested in an acid environment to simulate the acid released from the decomposition products of RDX [3].

Although extensive work on the development of better LOVA propellants has been done over the past several years [1], and as a result some useful formulations have been found, considerable room for improvement still exists. The sensitivity, to unintentional ignition, of a candidate TPE cannot be adequately determined unless it is tested and the results, whether or not this TPE appears promising, can provide useful information on the development of future formulations.

1.3 A NEW APPROACH TO THE DEVELOPMENT OF LOVA PROPELLANT BINDERS

Binders for LOVA propellants are usually made from macromonomers and a suitable monomer, for example, polystyrene macromonomers and n-butyl acrylate or methoxy ethyl acrylate. These monomers are then copolymerized to create a graft copolymer [5], as depicted in Figure 1.1.

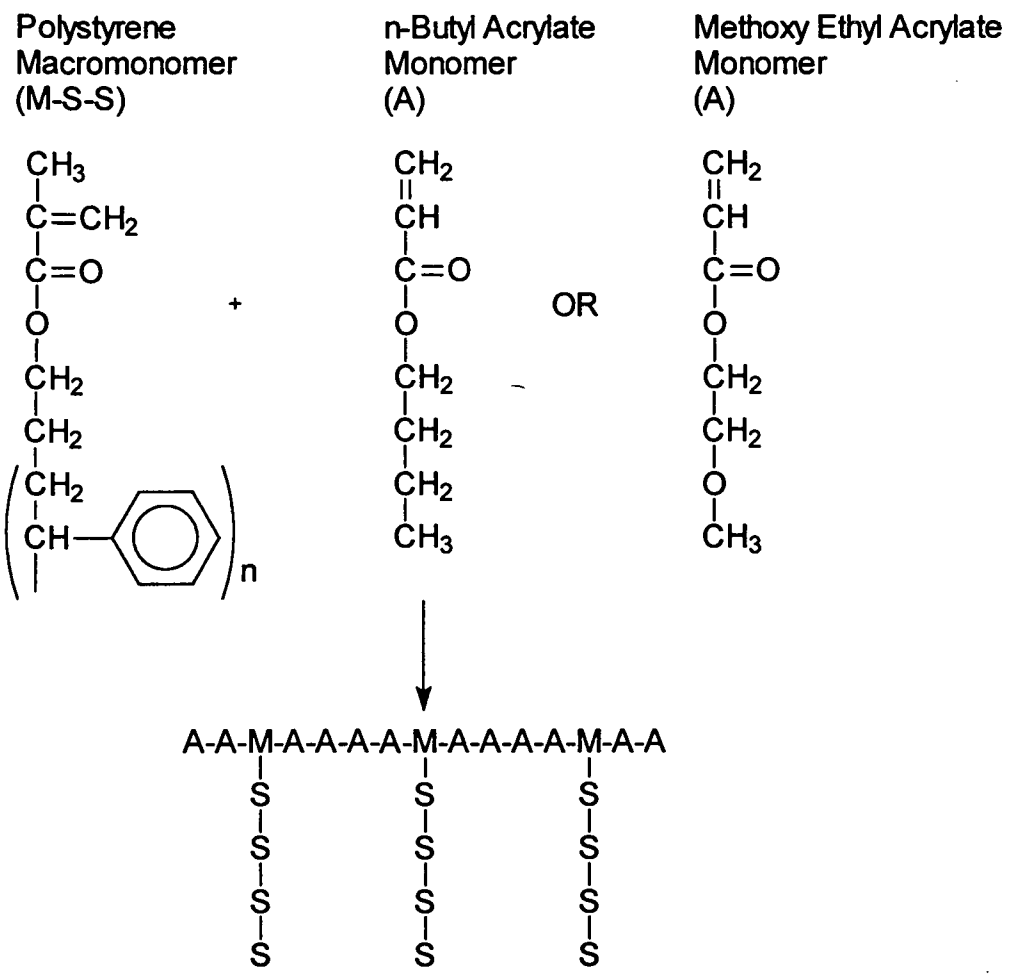

Figure 1.1: Copolymer formulations of polystyrene macromonomer and n-butyl acrylate or methoxy ethyl acrylate monomer.

A new and much less expensive approach than the macromonomer approach has been followed in this study to create the graft copolymer. The graft site was created by the reaction of acrylic/methacrylic acid with the epoxy ring of ENR. Methyl methacrylate was then polymerized onto the acrylic/methacrylic acid to create a graft copolymer, as shown in Figure 1.2.

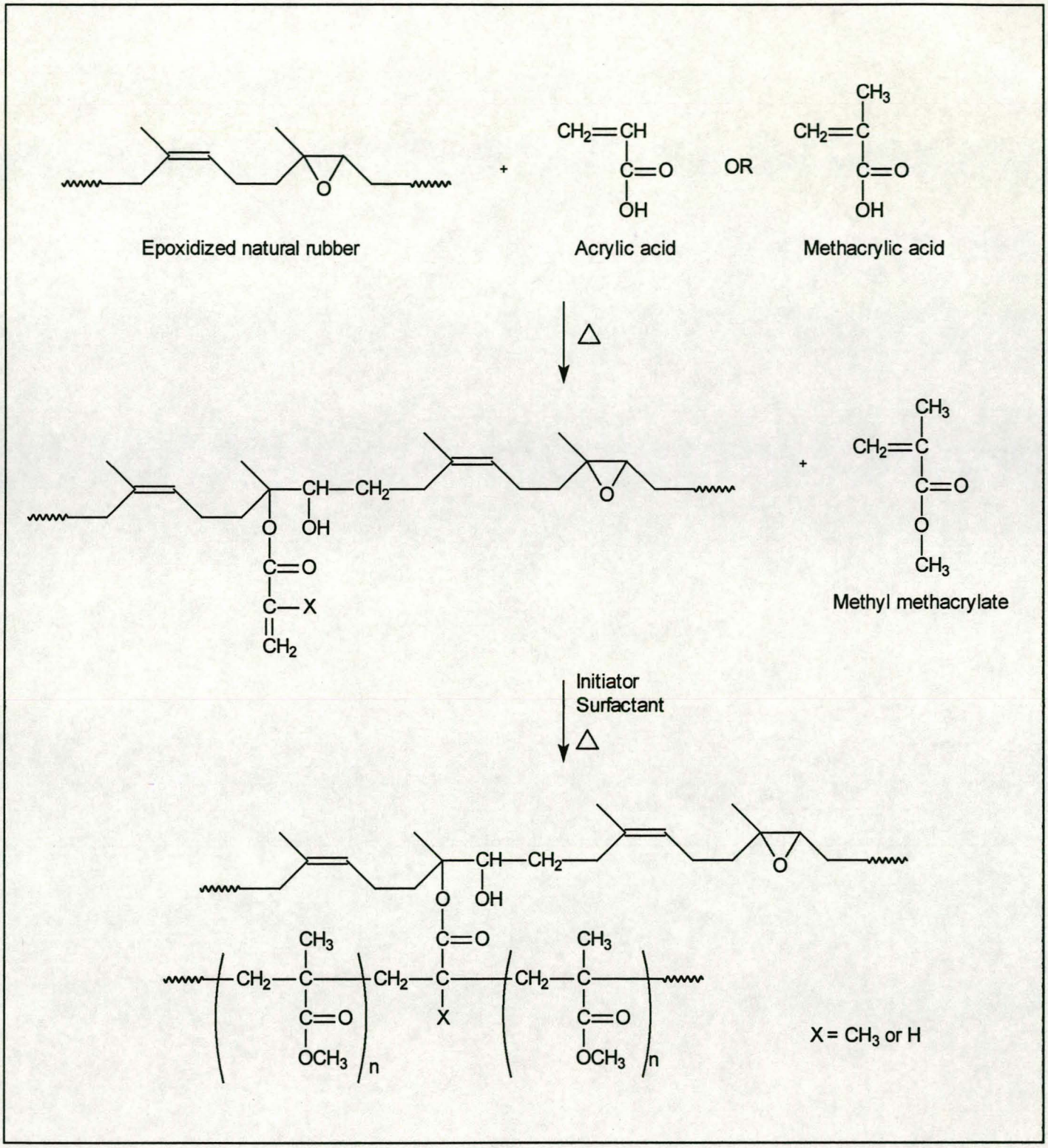

Figure 1.2: Chemical modification and grafting of epoxidized natural rubber.

1.4 ADVANTAGES OF USING EPOXIDIZED NATURAL RUBBER AS A SUBSTRATE FOR GRAFTING

The advantages of using ENR include [4]:

- It is a very versatile rubber.
- It has enormous dampening properties compared to natural rubber.
- It is highly reactive due to the presence of the epoxy group and can therefore act as an acid scavenger (stabilizer) as well as fulfill its role as binder.
- It is commercially available.
- It is oxygen rich and that will enhance the release of energy in the propellant and hence its effectiveness.

1.5 OBJECTIVES OF THIS RESEARCH

- A prerequisite of this research was to carry out a full literature study on ENR and emulsion graft-polymerization techniques.
- To graft epoxidized natural rubber in latex form with a vinyl monomer (MMA was selected). To date, no attempt has been made to do this. This was to be done using a novel method which entailed the use of an acrylic or methacrylic acid to create the graft sites for further polymerization reactions (see Figure 1.2).
- To synthesize a thermoplastic elastomer that will have dampening properties at low (about -25 °C) and high (about 80 °C) temperatures. I aimed at using ENR50 and MMA to make this thermoplastic binder.
- To obtain a greater understanding of the process of grafting of MMA onto ENR.
- To use the Perkin-Elmer DMA 7e Dynamic Mechanical Analyzer and the Eumetric System III Microdielectrometer, both separately and simultaneously, as analytical tools to obtain results which could be used to select the right grafting conditions (as detailed in Chapters 3 and 5) and to optimize the grafting reaction, e.g. type of acid used for graft site formation, type of surfactant and amount of monomer used.
- To carry out extensive dynamic mechanical and dielectric studies, both separately and simultaneously, in order to establish phase separation of ungrafted rubber and grafted PMMA.

- To determine the impact strength of the grafted material by calculating the area under the loss moduli curves. The use of loss moduli curves for impact resistance determination has only been done once on the Perkin-Elmer DMA 7e [6].

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CHAPTER 2

HISTORICAL AND LITERATURE REVIEW

2.1 HISTORY OF EPOXIDIZED NATURAL RUBBER

The commercial viability and the potential applications of epoxidized natural rubber (ENR) were only fully realized in the last decade or so. During the 1920's to 1970's it was shown that good yields of epoxides were generally obtained when using perbenzoic acid [1, 2], chloroperbenzoic acid [3, 4] and monoperphthalic acid [5]. If peracetic acid is used, the products depend on the medium of reaction. In inert organic solvents good yields of epoxides were obtained while in acetic acid the hydroxyacetates were formed [6, 7] because the epoxide first formed is easily ring-opened in acidic media.

Performic acid is an extremely active organic peracid [7] but, owing to its instability [8], it has to be prepared *in situ*. Epoxidization of olefinic compounds is thus generally conducted in the high acidity medium of formic acid and the chief products are the hydroxyformates [9]. Until the late 1970's, most of the epoxidization reactions of performic acid were performed with simple olefinic compounds or with solutions of low molecular weight unsaturated polymers.

Natural rubber (NR) was first epoxidized in 1922 [10]. However, until recently, there was little available on the properties of the products and, in some cases, the results were conflicting. The solution epoxidization of other unsaturated polymers has been reviewed by Greenspan [11]. In 1981 Ng and Gan studied the performic acid epoxidization of **natural rubber latices**. This was done because of the suitability of the aqueous latex as a medium for the reaction with performic acid. They also hoped that the introduction of polar groups into hydrocarbon polymers might yield modified polyisoprene, with interesting properties. This attempt to epoxidize natural rubber with performic acid generated *in situ* was only successful up to about 7 mol % epoxidization, beyond which coagulation and ring-opening side reactions occurred [12].

The chemistry of the epoxidization of unsaturated compounds and subsequent ring-opening reactions have been extensively studied [13, 14]. Epoxidization is a

stereospecific process [15], and its rate is governed by the substituents on the double bond [16]. Neighbouring groups control the ease and position of ring-opening of epoxides; therefore both electronic and steric factors are important [17]. Acidity and temperature of the reaction medium appear to be the main factors that govern the nature of the product from the reaction of natural rubber with peracids. At high acid strength and/or temperature the major products are derived from secondary ring-opening reactions [12, 18]. However, epoxidized natural rubber can be obtained under milder conditions [19]. In 1982 Gelling patented a method of making epoxidized cis 1,4-polyisoprene and in 1985 he showed that any desired degree of pure epoxidization was possible under controlled conditions. A pilot plant was then set up in Malaysia to manufacture three grades of ENR, i.e. ENR 10 (10 mol % of the rubber double bonds are epoxidized), ENR 25 (25 mol %), and ENR 50 (50 mol %). The three grades were made available in small tonnages as development products until they were commercialized in 1988. However, ENR 10 was later withdrawn, because it behaved much like natural rubber. ENR is now commercially available under the tradenames Epoxyprene 25 and Epoxyprene 50.

2.2 POTENTIAL APPLICATIONS OF EPOXIDIZED NATURAL RUBBER

Epoxidization is perhaps the only known chemical modification of NR, apart from cis-trans isomerization, where the products remain elastic above 20 mol % modification. Many chemical modifications of NR e.g. chlorination, led to resinous materials with no elastic properties [20, 21]. From this viewpoint, ENR is a rubber with many interesting properties, if manufactured free of side groups which could be formed as a result of secondary ring-opening reactions. Increasing epoxidization increased the glass transition temperature, which resulted in decreased resilience (more damping), reduced air permeability, higher hysteresis, and better wet traction. The epoxidization increased the polarity, which brought about an improved resistance towards hydrocarbon oil [22-24]. Because of these attributes, ENR may be utilized in many areas of application as is shown in Table 2.1. [25].

Table 2.1: Potential applications of ENR [25].

Features	Applications	Recommended grade
Oil resistance, high strength	Hoses, seals, Blow-out preventors, Connector and tubes	ENR 25, ENR 50
Low gas permeability	Bladders, inner tubes, and tyre liners	ENR 25
Silica reinforcement	Where black is not Acceptable and high Reinforcement is required	ENR 25
Wet grip, low rolling resistance	Tyre treads, non-slip flooring, sports shoe soles	ENR 25, ENR 50
Damping	Anti-vibration mountings and other engineering applications	ENR 25, ENR 50
Adhesion	Adhesives, cover for PVC conveyor belt	ENR 25, ENR 50

The presence of epoxy groups in ENR also opens opportunities to explore concepts such as macromolecular antioxidant, novel crosslinking systems, and silane-silica reinforcement. The introduced polarity makes the rubber more versatile for rubber-rubber or rubber-plastic blending, especially in the area of thermoplastic elastomers.

2.3 PREPARATION OF ENR

Several reports have been described on the preparation of ENR gum from NR latex [26-28]. In a typical production, the latex is first stabilized with a non-ionic surfactant e.g. fatty acid/ethylene oxide condensate, and then reacted with a peracid, usually performic or peracetic acid. The peracetic can be synthesized separately, or formed *in situ* from a precursor acid and hydrogen peroxide. The latter is preferred commercially because of the instability of the peracid at room and higher temperatures. A typical process of obtaining ENR gum via *in situ* epoxidization is outlined in Figure 2.1.

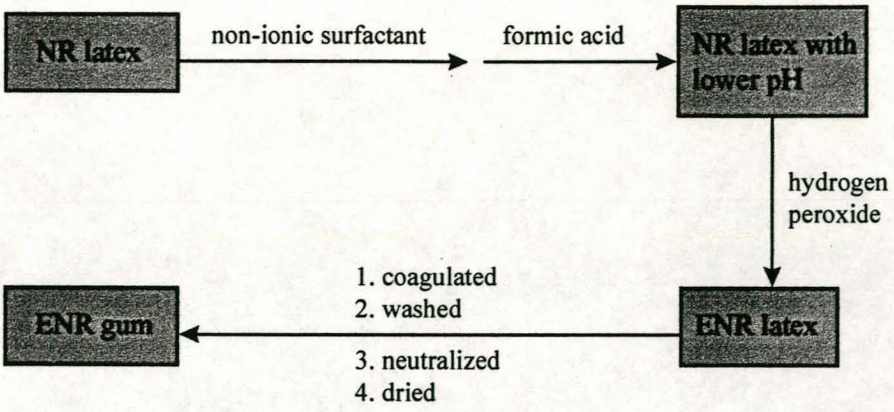
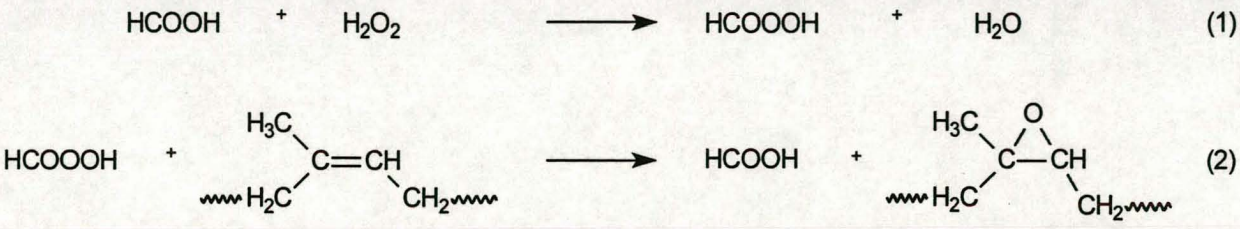


Figure 2.1: A typical process of ENR preparation from NR latex via *in situ* epoxidization with formic acid and hydrogen peroxide.

When epoxidization is carried out *in situ*, two consecutive reactions are involved i.e.



Reaction (1) has been found to be the rate-determining step with an activation energy of 55 ± 6 kJ/mol [26]. In another study of epoxidization with preformed peracetic acid, the overall activation energy was found to be 56.2 kJ/mol [27].

Unless a lower degree of epoxidization is required, addition of a surfactant is necessary to prevent the latex from coagulating during epoxidization. The latex would be stable from a few hours to several days, depending on the amount of surfactant added, and a few other factors such as the acidity of the latex prior to titration. Up to 90 mol % epoxidization is possible by changing parameters such as dry rubber content of the latex, hydrogen peroxide/acid ratio, and reaction temperature and duration. Some reaction conditions to obtain moderate to high degrees of epoxidization, free of side groups, have been established and are listed in Table 2.2. [25].

Table 2.2: Some reaction conditions for the *in situ* epoxidization of NR latex (hydrogen peroxide/formic acid system) [25].

	Reference	Temperature (°C)	Dry rubber Content (wt %)	H_2O_2/Acid Mol ratio	Reaction time (h)	Maximum epoxidization (mol %)
1	26	3	24	0.46	32	40
2	28	RT	20	0.53 - 3.54	30 - 70	90
3	29	RT	58	3.3 - 1.3	60 - 120	70 - 80
4	29	50	27 - 58	5.0 - 13.0	12 - 14	55 - 57
5	30	50	20 - 40	1.5 - 3.0	9 - 12	60

Once the desired degree of epoxidization is achieved, the rubber is coagulated with methanol (or aqueous methanol), thoroughly washed with distilled water, then neutralized with a sodium carbonate solution, and finally rinsed with distilled water again to ensure that any remaining acid is removed. The rubber is then dried to constant weight, usually in a vacuum oven at a moderate temperature.

Instrumental techniques or chemical techniques are used to determine the degree of epoxidization. Titration with HBr, tetraethyl ammonium bromide/perchloric acid, or HCl, provides a simple and fast method of determining ENR with a low degree of epoxidization [31, 32]. For ENR with higher degree of epoxidization, accuracy demands that instrumental techniques such as NMR spectroscopy be used [32].

2.4 PROPERTIES OF ENR GUM

2.4.1 Structure and stereoregularity

Based on ^{13}C-NMR analysis, the epoxy groups were found to be non-randomly distributed regardless of epoxidization levels [33]. Epoxidization was also found to be a stereospecific reaction i.e. cis-olefin undergoes cis-epoxidization [34]. Thus, the cis 1,4 configuration of NR is maintained in ENR.

2.4.2 Glass transition temperature

The higher the mol % epoxidization in ENR, the higher the T_g as shown in Figure 2.2.

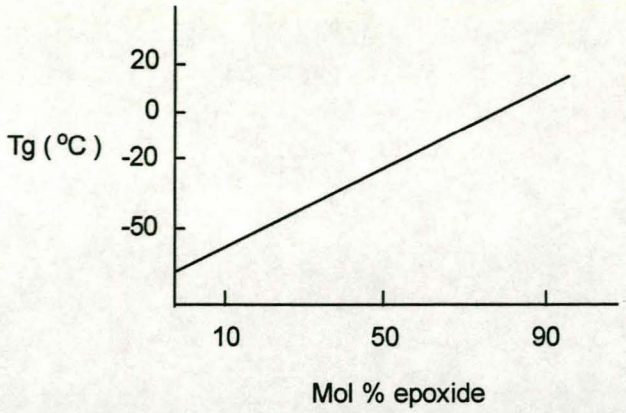


Figure 2.2: The effect of mol % epoxidization in ENR on T_g [25].

The higher T_g is partially responsible for maintaining the high tensile properties of ENR [35]. Increased T_g is also responsible for a decreased resilience and air permeability of the rubber.

2.4.3 Solubility behaviour

Due to the introduction of polar groups into the rubber it becomes sensitive to polar solvents and less soluble in non-polar solvents. The solubility and gelling behavior of ENR in various solvents has been studied [29, 31] and it was found that an increase in epoxidization leads to an increased gel content i.e. the insoluble portion of the rubber.

2.4.4 Molecular weight

The molecular weight determination is complicated by gel formation during epoxidization. However, GPC measurements made on the soluble portion indicated that the molecular weight decreases with increasing epoxide levels [29]. No mechanistic mechanism for the decrease in molecular weight has yet been offered, but chain scission of the rubber molecules via a radical pathway is a possibility, since H_2O_2 was present in the system. This is especially true for products formed at higher reaction temperatures.

2.4.5 Storage stability

ENR is expected to be more stable than NR with respect to air oxidation since it contains less unsaturation. This was confirmed by a study [36] which reported that NR samples underwent greater oxidation than ENR samples at room and higher temperature. The residual acidity of ENR has been a concern and a special precaution was recommended during the compounding and processing [23]. This suggested that the acidity of ENR could be a critical factor for the storage stability. However, it was found that ENR is fairly stable in its latex state. Only a small amount of the epoxide groups underwent ring-opening and were converted to diols when the latex was boiled under mildly acidic or alkaline pH [37]. At low temperatures, ENR was found to be resistant to crystallization and this behaviour improved as epoxide levels increased [23].

2.5 REACTIVITY AND CHEMICAL MODIFICATIONS OF ENR

2.5.1 Reactivity of epoxy groups

The epoxy groups are susceptible to attack by acids, which include any residual acid used for epoxidization. Protonation of the epoxy groups by acid could cause ring-opening reactions leading to the formation of diols, ether crosslinks, or tetrahydrofuran rings [25].

2.5.2 Chemical modifications via epoxy groups

The epoxy groups in ENR are reactive sites for further modification, or they can be used as crosslinking sites. Besides the reactivity with acid, ENR can react with compounds containing amino functional groups. The ability of ENR to react with such functional molecules has been substantiated by a few reports [20, 21]. The reaction of epoxidized 1,4-polyisoprene with aromatic amines has been the subject of a few studies aimed at the synthesis of polymer-bound or macromolecular antioxidant. Polymer-bound aromatic antioxidants containing amino groups are of further interest due to their better efficiency as antioxidants and reduced toxicity [38]. The reaction, which could be carried out in solution or latex phase, involves ring-opening of the epoxy groups. See Figure 2.3.

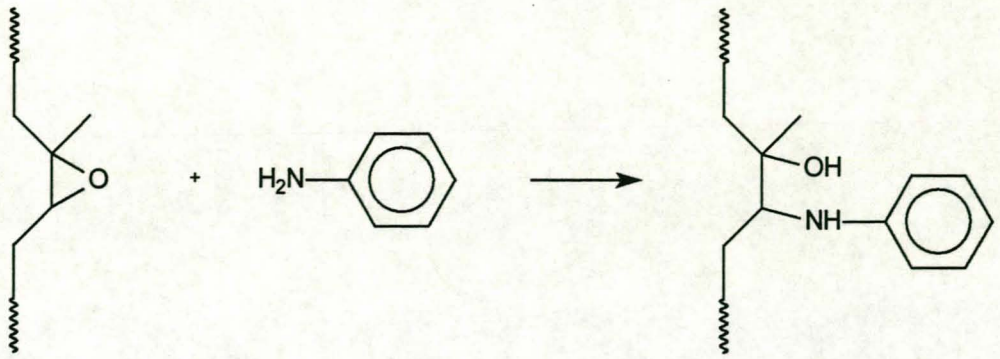


Figure 2.3: Reaction of ENR with an aromatic amine.

Amines react with epoxidized rubber in the presence of a catalyst, but at a considerably lower rate than carboxylic acids [39]. Prior studies have shown that carboxylic acids react with epoxidized rubber to form esters [40]. Epoxides can also react with *acrylic* (or *methacrylic*) acid to form epoxy *acrylate* (or *methacrylate*). Theoretically speaking, almost any epoxide group can be acrylated given the right conditions as has been reported by Holman [41]. There are several important factors that govern the reaction between ENR and acrylic (or methacrylic) acid. These factors need to be monitored in order to minimize the risks of gelation during synthesis.

The most important ones were found to be:

- reaction temperature
- inhibitor
- catalyst
- reactant ratio
- concentration of ENR
- reaction time.

The chemical modification of ENR by acrylic acid or methacrylic acid has been done in solution reactions. The method used in this research will entail the use of ENR as it is provided in latex form and an emulsion polymerization technique will be utilized.

2.6 STABILITY OF LATICES

2.6.1 Requirements for stabilization

The ENR used was in latex form. Latex (plural: latices) is a colloidal system, the dispersed phase of which is polymeric in character. To understand the grafting of ENR and its effect on the ENR latices, it is necessary to understand the stability of the ENR latices. Given that there exist strong, long-range attractive forces between colloidal particles, it follows that in order to impart colloid stability, it is necessary to provide long-range repulsion between the particles. This repulsion must be at least as strong as, and comparable to the attractive interaction.

2.6.2 Current stabilization methods

The number of options that are available for stabilizing colloidal dispersions is severely limited. There currently exists only two general ways by which colloid stability can be imparted: *electrostatic stabilization* and *polymeric stabilization*.

2.6.2.1 Electrostatic stabilization

The paramount difficulty in this stabilization method resides in the projection of the repulsion over distances comparable to that of the attraction (5-10 nm). One way to accomplish stabilization is to use Coulombic repulsion. In the electrostatic stabilization of aerosols, the Coulombic repulsion between the colloidal particles is of a long-range character and can impart stability. In liquid dispersion media, however, the principle of electroneutrality demands that the net charge in the dispersion medium be equal, but opposite in sign, to that of the particles. The counterions in the dispersion medium give rise to the electrical double layers that surround the colloidal particles. It is the mutual repulsion of these double layers that provides stability in electrostatic stabilization.

2.6.2.2 Polymeric stabilization

There are different types of polymeric stabilization, namely steric and depletion stabilization.

Steric stabilization. Steric stabilization of colloidal particles is imparted by macromolecules that are attached (e.g. by grafting or by physical adsorption) to the surfaces of the particle. This is represented schematically in Figure 2.4.

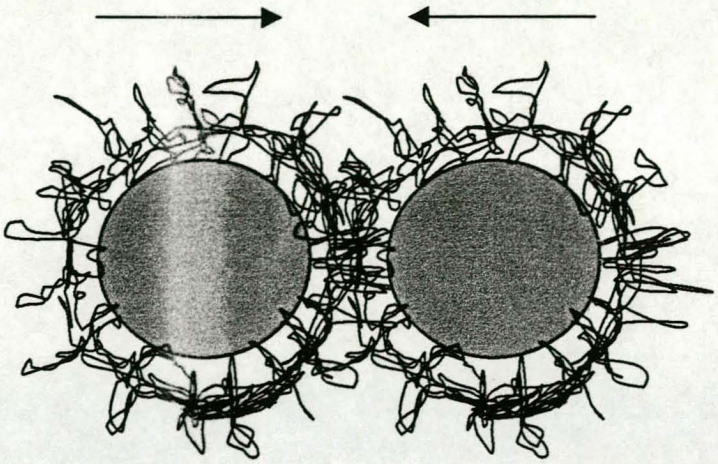


Figure 2.4: Schematic representation of steric stabilization.

Depletion stabilization. This differs from steric stabilization in that stability is imparted not by attached polymer but rather by macromolecules that are free in solution. See Figure 2.5.

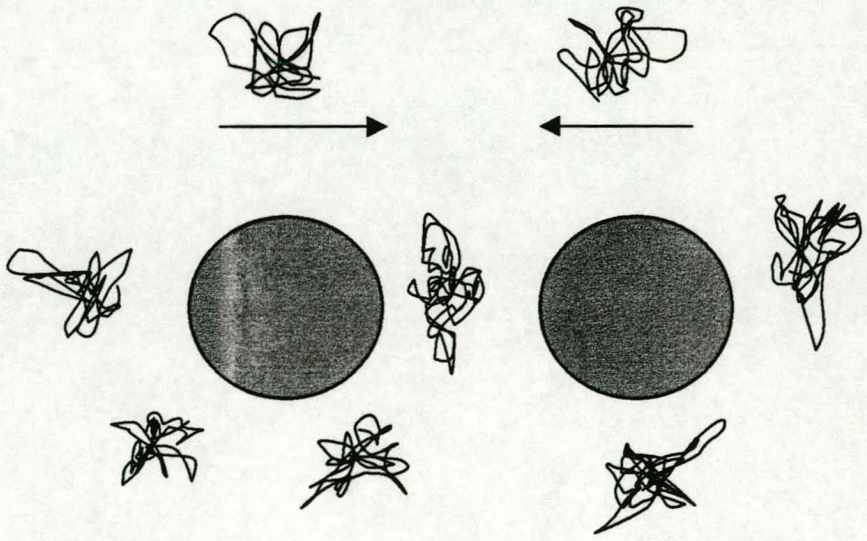


Figure 2.5: Schematic representation of depletion stabilization.

2.6.3 Combinations of stabilization methods

2.6.3.1 Electrosteric stabilization

It is possible to have combinations of electrostatic and steric stabilization, which has been termed *electrosteric stabilization*. The electrostatic component may originate from a net charge on the particle surface (see Figure 2.6a) and/or charges associated with the polymer attached to the surface as those from an attached polyelectrolyte (see Figure 2.6b). Electrosteric stabilization is common in biological systems.

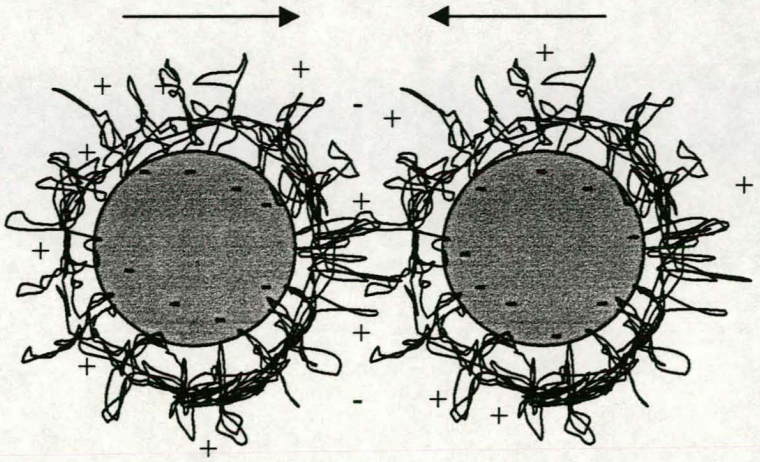


Figure 2.6a: Representation of charged particles with nonionic polymers.

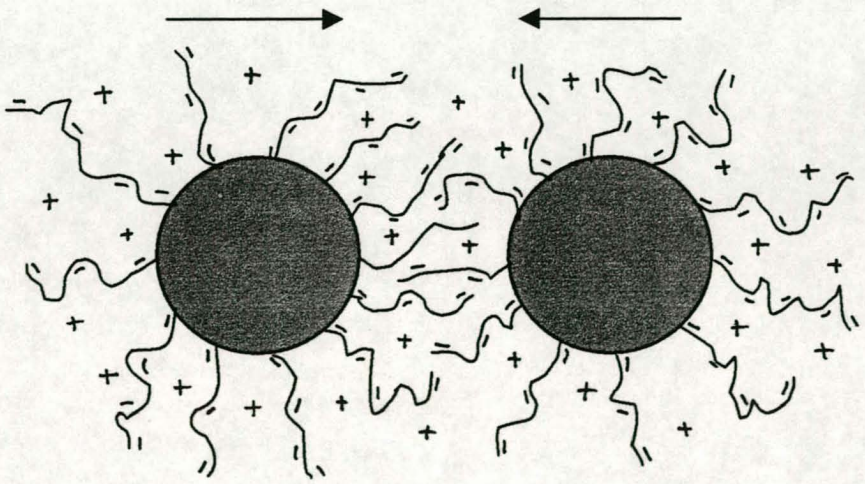


Figure 2.6b: Representation of polyelectrolytes attached to uncharged particles.

2.6.3.2 Other combinations

In addition to electrosteric stabilization, it is possible to have combinations of depletion stabilization with both steric and/or electrostatic stabilization. The combination of depletion and steric stabilization is quite common at high concentrations of free polymer in the dispersion medium.

2.6.4 The effects of polymer on colloid stability

Some of the effects that polymers produce on colloidal dispersions are summarized in Table 2.3. This table illustrates dramatically the enormous complexity of the effects that polymer chains can exert on colloidal dispersions, e.g. latices. Some 13 phenomena are already well documented and this list is likely to be expanded in the near future as additional diverse phenomena are discovered [42].

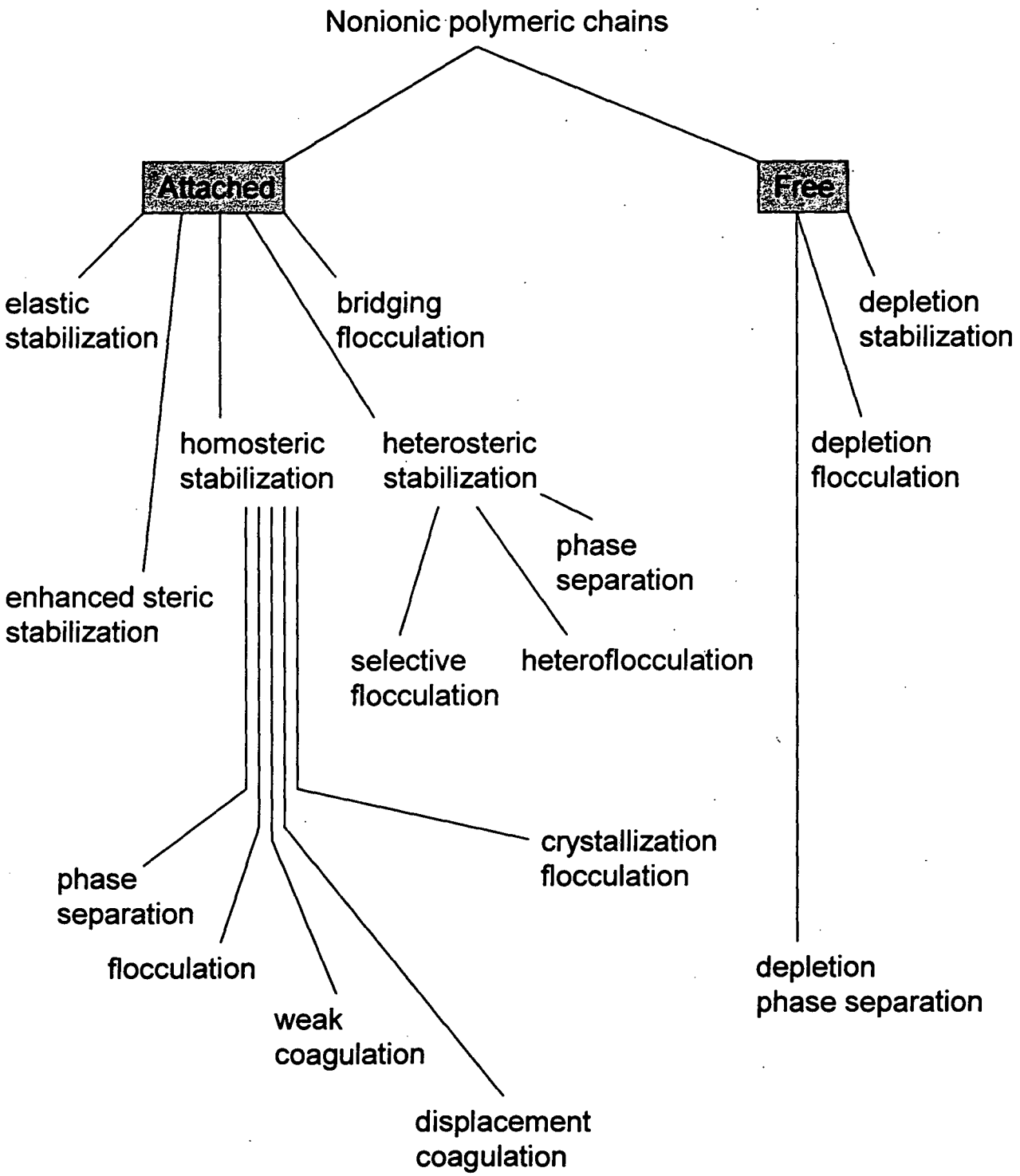
2.7 EMULSION POLYMERIZATION FOR THE GRAFTING OF ENR

Emulsion polymerization has been known since the early twentieth century; the first patent was issued to the Bayer Company in 1909. Developments continued slowly but the fundamental elements of the technology were known by the beginning of World War I. In spite of this, no discernible emulsion polymer industry existed at that time. By 1930, however, the technology had been fairly well developed and the decade of the thirties saw the beginning of the synthetic industry.

Further development of the industry would likely have been slow, had it not been for the beginning of World War II and probably the ensuing inability of the industrial nations to obtain natural rubber. This saw the rapid development of the emulsion polymer industry. Further expansion of the emulsion polymer industry had however to await the end of the war, but once this occurred the industry quickly grew to encompass a myriad of applications. Emulsion polymers have become critical raw materials in the manufacture of a wide variety of nondurable products, among which are coatings, adhesives, paper, carpets, foams, textiles, both conventional and nonwoven.

Simply defined, a latex or emulsion polymer (the two names are usually used synonymously, although they are not strictly such) is a dispersion of polymer particles in

Table 2.3: The effects of polymers on colloidal dispersions.



water. That definition is an oversimplification, however, since dispersions of polymers made by means other than emulsion polymerization can be prepared. Emulsion polymers may contain a large number of ingredients, but only water, monomer, initiator and surfactant are essential to the process.

2.7.1 Techniques for emulsion polymerization

While it is true that only a few ingredients are needed to make latex, and the total number present in any given recipe is always held to a minimum, there are an infinite number of ways in which these components can be assembled. This makes the latex very technique-sensitive and explains the very proprietary nature of the emulsion industry. These techniques can be categorized, thus allowing a systematic examination of the process. But it should be remembered that there are subdivisions of each category, of which the number and nature are only limited by the imagination of the researcher.

2.7.1.1 Batch process

In the batch process, just as the name suggests, all the ingredients are added initially and the reaction allowed to proceed to completion while agitating. This requires considerable control, since the reaction is exothermic. If the heat is not removed as it is released, an uncontrolled reaction will occur in which the boiling point of water is reached, leading to pressure increase and a violent release of the reactor contents. Adequate cooling is therefore required to dissipate the heat of polymerization. This process is most readily used for the preparation of styrene-butadiene latices because of the slower reaction rates involved. The emulsion polymer formed will generally exhibit small particle size and high viscosity. This is a result of the high initial surfactant concentration, which causes the generation of many particles in the initial stages of the reaction [41].

2.7.1.2 Delayed addition of monomer

Violent reactions such as in the batch process can be avoided if the quantity of unreacted monomer is kept at a minimum. To do so, a portion or all of the monomer is added continuously, or incrementally, throughout the polymerization process. This allows better control of the exotherm resulting from the monomer reaction and is

particularly suited for fast reaction monomers such as acrylate esters and their copolymers. The monomer is added at a controlled rate over a pre-determined period of time, usually a few hours. The content of the reactor is therefore, not more than a few percent monomer, and the amount of monomer can be maintained at a level below the rate of consumption.

One modification of this procedure requires the initial charging of ten to twenty percent of the monomer followed by continuous addition of the remainder throughout the course of the reaction. Another modification utilizes incremental addition of monomers in three or more stages. Generally, delayed monomer addition results in small particle-size emulsions, since a large excess of surfactant is present when particle initiation takes place. The delayed addition of monomer has the further advantage of creating a more 'nearly random' distribution of monomer units in copolymers (if desired) [41].

2.7.1.3 Delayed addition of monomer and surfactant

In this procedure a portion of the monomer(s) and surfactant(s) are added to the reactor initially and the remainder continuously throughout the reaction. In this way, a large excess of surfactant is avoided during the particle formation step and a latex with a somewhat larger particle-size results. Particle size distribution can also be changed if sufficient surfactant is added to generate new micelles, thus creating new particles which now have shorter time in which to attain their maximum size and will thus be smaller than the others [41].

2.7.1.4 Pre-emulsion of monomer

In this procedure, the monomer(s), surfactant(s) and a portion of the water are added, as a preformed emulsion, throughout the course of the polymerization. This has the effect of introducing both monomer and surfactant into the reactor in the precise ratio that they will be present in the final latex. Since excess surfactant is maintained at a low, and relatively constant level, the particle size of the resultant latex tends to be uniform and relatively large. This approach has been found helpful in incorporating water soluble specialty monomers such as N-methylol acrylamide or hydroxyethyl methacrylate into emulsion polymers, since the aqueous phase concentration of the specialty monomer is kept low throughout the polymerization [41].

2.7.1.5 Seeding techniques

During this procedure seed latex is either charged to the reactor as preformed latex, or is formed *in situ* in the first stage of a two-stage polymerization. To the seed latex is added additional water, followed by the continuous addition of surfactant(s) and monomer(s). This approach allows the formation of latices having bimodal or polydispersed particle sizes, with large particles arising from the growth of the initial seed particles and smaller particles generated during the second stage of the polymerization. Uniform particle size polymers can also be made using seeding techniques [41].

2.7.2 The role of surfactants in the emulsion polymerization process

The surfactant used in the emulsion polymerization process is sometimes simply referred to as "soap", and it is both the boon and the bane of emulsion polymerization. It is essential in the sense that it increases the water solubility of the monomer and provides the necessary stability for the final product [43].

A wide variety of surfactants are used in emulsion polymerization. In general, surfactants contain both polar (hydrophilic) and non-polar (hydrophobic/lipophilic) groups. This dual nature of surfactants provides to its functionality in the sense that it enables the surfactant to form stable emulsions of monomers in water. A surfactant's ionic nature is determined by its chemical structure. In emulsion polymerization work the emphasis is on anionic and nonionic surfactant chemistry, rather than cationic surfactant chemistry.

Examples of anionic surfactants are:

Sulfonic Acid Ester salts	
$C_{12}H_{25}OSO_3\text{-}Na^+$	sodium laurylsulphate
Sulfonic Acid salts	
$C_{12}H_{25}\text{-}Ph\text{-}SO_3\text{-}Na^+$	sodium dodecylbenzene sulphonate
Phosphoric Acid Ester	
$C_{13}H_{27}O(CH_2\text{-}CH_2\text{-}O)n\text{-}PO_3H$	tridecyl ethoxy phosphate

Examples of nonionic surfactants are:

$C_{12}H_{25}O(CH_2\text{-}CH_2\text{-}O)nH$	ethoxylated lauryl alcohol
$C_9H_{19}\text{-}Ph\text{-}O(CH_2\text{-}CH_2\text{-}O)nH$	ethoxylated nonyl phenol

Nonionic surfactants do not have an ionic charge; the surfactant properties come from the extended polar portions within the molecule.

Within the nonionic surfactant family there are several lipophilic groups which form a homologous series (such as the nonyl phenol-based series) and which then contain various levels of ethylene oxide (ethoxylation) which change the properties, within that series. The ethoxylation number directly influences the viscosity, foam generation, surface tension, cloud point and solubility within any given lipophilic homologous series. An increase in this number will lead to an increase in the properties listed above.

When surfactants are discussed, it is common to refer to "moles of E.O." (ethylene oxide) in a particular surfactant. Surfactant NP9, for example, contains 9 moles of ethylene oxide on a nonyl phenol lipophile.

2.7.2.1 Hydrophilic / Lipophilic balance (HLB)

Physical properties of surfactants can also be expressed by the HLB value. This number is determined by the ethylene oxide content (as a percent) of the surfactant [44]. Taking the percentage ethoxylation of a nonionic surfactant and dividing it by five can approximate the HLB. In the case of NP9, the HLB is 13. The HLB scale is applied solely to nonionic surfactants.

Example: Calculate HLB of NP9.
Ethylene oxide weight: 9 moles x 44/moles = 396
Nonyl phenol weight = 220
Total surfactant weight = 616
Percent ethylene oxide 396 / 616 = 64,3 %
HLB = % E.O. / 5 = 64.3 / 5 = 12.9 ≈ 13

2.7.2.2 Function of surfactants in emulsion polymerization

Surfactants provide three functions in emulsion polymerization:

- Reduce interfacial tension between monomers and the aqueous phase to yield a stable dispersion or emulsification of the reactive and continuous phases.
- Provide the micellar reaction site for polymerization through the micelle formation concept.
- Stabilize the emulsion of unreacted monomer and growing polymer particles and, ultimately, the polymer latex emulsion.

The selection of a surfactant is governed by the effect it has on the required properties of the latex. These include particle size, viscosity, and mechanical stability and water sensitivity.

As it has been mentioned earlier (Section 2.7.2) the unique properties of surfactants are the result of their dual nature, namely a hydrophilic (water-soluble) portion combined with a lipophilic (oil-soluble) portion, in the same molecule. This dual nature means that the molecule will seek areas where both the hydrophile and lipophile can exist in a comfortable environment. The simplest location of this nature is an interface. When dissolved in water, the surfactant tend to aggregate at the air/water interface and align itself with their lipophilic portions oriented outwardly toward the air and their hydrophilic portions directed inwardly into the aqueous phase. The effect of this surface-excess of surfactant is to disrupt the water structure at the surface and results in a lowering of the surface tension. See Figure 2.7.

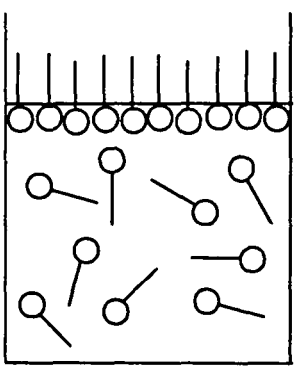


Figure 2.7: Surfactant molecules at the air/liquid interface.

If the interface is the surface of droplets, an emulsion is formed and it is stabilized by the surfactant. Solids can be similarly stabilized. In this case the lipophile is absorbed on the surface of the solid and the hydrophile extends into the water. This situation exists in latex. See Figure 2.8.

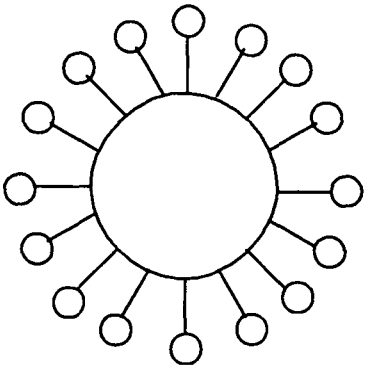


Figure 2.8: Schematic representation of the stabilization of a polymer by a surfactant.

The extended hydrophiles stabilize the dispersion either by electrostatic repulsion in the case of ionic surfactant or by steric exclusion in the case of nonionic surfactants. Surfactants can exist in locations other than interfaces, however. The surfactant molecules may attain a lower energy state by aggregating into clusters, called micelles, in the aqueous phase. Micelles consist of hydrophobes that associate in such a manner as to exclude water and form an essentially organic domain. The structure of these micellar aggregates is roughly spherical, and is comprised of between 50–100 surfactant molecules aligned with their lipophilic portions pointed inwardly.

These organic domains will dissolve other organic substances. It is this phenomena that increases the solubility of the monomers in emulsion polymerization and which provides a site for a growing polymer chain. As the concentration of surfactant in the aqueous phase increases, so does that in the interfacial layer. When this layer becomes saturated, there is no further change in surface tension with increasing surfactant concentration in the aqueous phase (i.e., surface tension is at a minimum and remains constant with increased surfactant concentration).

This point, at which any increase in the aqueous phase concentration of surfactant results in the formation of new or larger micellar aggregates, is a unique property of each surfactant and is known as its critical micelle concentration (CMC). The CMC is an

important criterion in emulsion polymerization. Most surfactants are added above their CMC, since the micelle generated by the surfactant solubilizes the monomers and provides a site for rapid polymerization. The final particle size of a polymer is usually related to the efficiency (CMC) of the surfactant. The lower the CMC, the more efficient it is, and the smaller the particle-size of the emulsion. Anionic surfactants, in general, have a lower CMC value than those of nonionic surfactants and are therefore often used to generate small particle-size emulsions. CMC values, and therefore particle size, decreases within a homologous surfactant series as the amount of ethoxylation of a surfactant increases.

2.7.2.3 HLB considerations for nonionic surfactants

The HLB value of a surfactant is directly related to its water solubility. The higher the HLB value, the better the solubility. High HLB-value surfactants with high solubilities may not form micelles but instead generate immobilized clouds of water which congregate about the polymerization site and subsequent polymerization particles. Very high HLB nonionics may therefore act like protective colloids.

In emulsion polymerization reactions the levels of surfactant used typically vary from 3-6% (based on the monomer content) for nonionics and 2% or less for anionics. As the concentration of surfactant increases, particle size decreases since more micelles are formed and a higher solids content results. Insufficient surfactant can result in coagulation and an unstable emulsion, while excess surfactant can result in poor water resistance.

Mixed systems of anionic and nonionic surfactants can also be used for emulsion polymerization and may result in excellent electrolyte stability, particle-size and pigment binding properties.

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CHAPTER 3

PRE-SCREENING EXPERIMENTS FOR THE REACTION BETWEEN EPOXIDIZED NATURAL RUBBER AND METHYL METHACRYLATE

3.1 INTRODUCTION

The epoxidized natural rubber was supplied with 50 mol % epoxide groups (ENR50) and a rubber content of 30% [1]. ENR50 was supplied in latex form and it was decided to use an emulsion polymerization technique [2] for the reaction of methyl methacrylate (MMA) with ENR50. Emulsion polymerization and the various related techniques have been described in detail in Sections 2.7.1 and 2.7.2. The problem with ENR50 is that the latex can easily be destabilized [3]. ENR50 is stabilized by natural proteins, to form a colloidal dispersion. The net charge of the proteins attached to the latex particles stabilizes the latex through electrosteric stabilization [3]. Any number of components or combinations of the components used, in the emulsion polymerization reaction of ENR50 and MMA, can disrupt these charges to lead to destabilization and grit formation. The influence of the surfactant on stability will be discussed later (Section 3.2.2). Three techniques were looked at for the emulsion polymerization reaction of ENR50 and MMA: a batch process, delayed addition of monomer and a pre-emulsion technique [2].

3.2 EXPERIMENTAL

3.2.1 TECHNIQUES USED FOR THE EMULSION POLYMERIZATION

3.2.1.1 Aim

The aim of these experiments was to find a suitable technique that could be used for the emulsion polymerization reaction that would not lead to destabilization of the latex.

3.2.1.2 Materials

The materials used are summarized in Table 3.1. See Table 5.3 for the amount of material used in the polymerization reaction of ENR50 with MMA with the use of MAA as graft site initiator.

Table 3.1: Materials used in the emulsion polymerization reactions between ENR50 and MMA.

Materials	Material Abbreviation	Supplier
Epoxidized natural rubber (50 % mol epoxy groups)	ENR50	Kumpulan Guthrie Berhad (Malaysia)
Methyl methacrylate	MMA	Plascon
Methacrylic acid	MAA	Plascon
Potassium persulphate	KPA	UniLab
Nonyl phenol50 (Surfactant)	NP50	Saarchem

3.2.1.3 Polymerization procedures

The technique used for emulsion polymerization must be selected carefully to ensure that the latex does not destabilize. Three procedures were looked at namely: batch polymerization, delayed addition of monomer and pre-emulsion of monomer. *Batch emulsion polymerization* required the addition of ENR50, water, surfactant (NP50), acid (MAA), monomer (MMA) and initiator (KPA) simultaneously into the reactor flask. The MMA is added last and small quantities are poured into the reactor at a time.

Delayed addition of monomer requires the addition of the ENR50, surfactant, acid and water into the reactor flask. MMA and the initiator are then separately added through the use of funnels to the flask over a period of 3.5-4h.

During the *pre-emulsion of monomer* a pre-emulsion of ENR50, MMA, surfactant, acid and water is made beforehand. The reactor flask is then charged with water, a small quantity of the pre-emulsion and with initiator. The rest of the pre-emulsion and initiator solution is then added over a period of 3.5-4h.

All of these reactions were performed under nitrogen at 82 °C and with a stirrer speed of 250 revolutions per minute.

The experimental set-up used is shown in Figure 3.1.

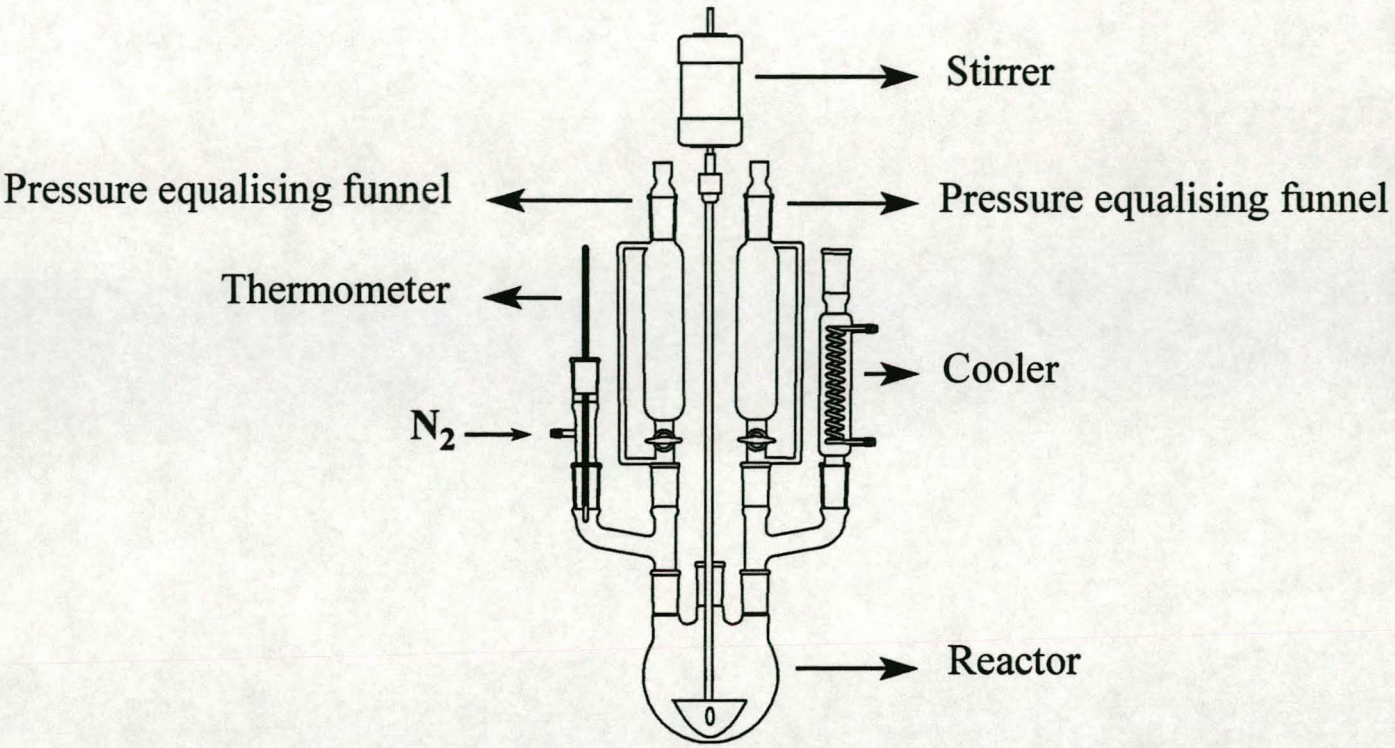

Figure 3.1: Experimental set-up used for the emulsion polymerization of ENR50 with MMA.

3.2.1.4 Results and discussion

Batch emulsion polymerization was not very successful. It did not matter how small the quantities of MMA were that are added at one time, there was always a period during which the MMA was enough to destabilize the latex. This method can only be successfully used if very small quantities of MMA are used during the whole reaction.

Delayed addition of monomer and the pre-emulsion techniques were used successfully during the polymerization of MMA with ENR50. These techniques are suitable for small to large quantities of MMA added, even where the ratio of ENR50 : MMA is 50 : 49 percent (based on the monomer weight). Results of polymerizations using these two techniques show different results on the tan delta peak of the material formed during the reaction of ENR50 with MMA. The results of using these two techniques on the T_g, where the formulations were kept the same, can be seen in Figure 3.2. The Perkin-Elmer DMA 7e dynamic mechanical analyzer measured the tan delta vs. temperature curves and the T_g was taken as the onset of the tan delta peak. Frequency was 1 Hz.

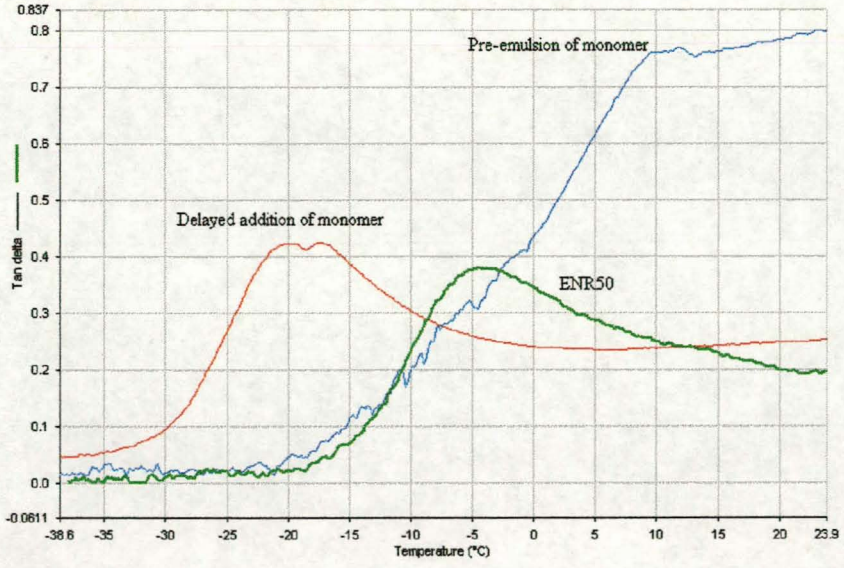

Figure 3.2: Tan delta vs. temperature curves to show the influence of the delayed addition of monomer and the pre-emulsion techniques used on the T_g.

Clearly the delayed addition of monomer led to a lower T_g and therefore a material that can be used at lower temperature. The pre-emulsion technique led to a material with a higher tan delta peak height value and will therefore have higher dampening properties. Therefore, depending on what you are looking for in a material, you can choose your preparation technique accordingly.

The shift of the T_g of the rubber peak to lower temperatures proves that the rubber is selectively epoxidized, i.e. it probably has a core in the latex particle with a lower degree of epoxidization. The reaction with MMA causes the low epoxidized rubber (with inherently lower T_g) to phase-separate from the higher epoxidized rubber blend with the grafted PMMA.

3.2.2 INFLUENCE OF SURFACTANTS ON THE STABILITY OF THE LATEX MADE BY THE PRE-EMULSION TECHNIQUE

3.2.2.1 Aim

The aim of these experiments was to determine the effect of surfactant on the stabilization of the latex.

3.2.2.2 Materials and polymerization procedure

The materials used were the same as those in paragraph 3.2.1.2. Both NP30 and NP50 were tested. The polymerization was done according to the pre-emulsion method. Polymerization reactions were done with 2%, 4%, 6% and 8% surfactant (based on the monomer weight).

3.2.2.3 Results and discussion

The stability was tested according to how much grit formation took place during the emulsion polymerization reaction. The results are summarized in Chart table 3.1. It is clear from the table that all the latex was destabilized when a surfactant of 2% was used (total destabilization is at about 36 g grit formed). The destabilization became less

pronounced as we proceed to 4% and 6%. At 8% surfactant, based on the monomer weight, basically no latex was destabilized. The amount of surfactant used is therefore of utmost importance in the reaction between ENR50 and MMA.

It can also be seen that the surfactant with the highest HLB value (NP50) shows less grit formation at corresponding levels of surfactant used. The reason is that the NP50 has a higher solubility-formation potential (see paragraph 2.7.2.3) and this results in a

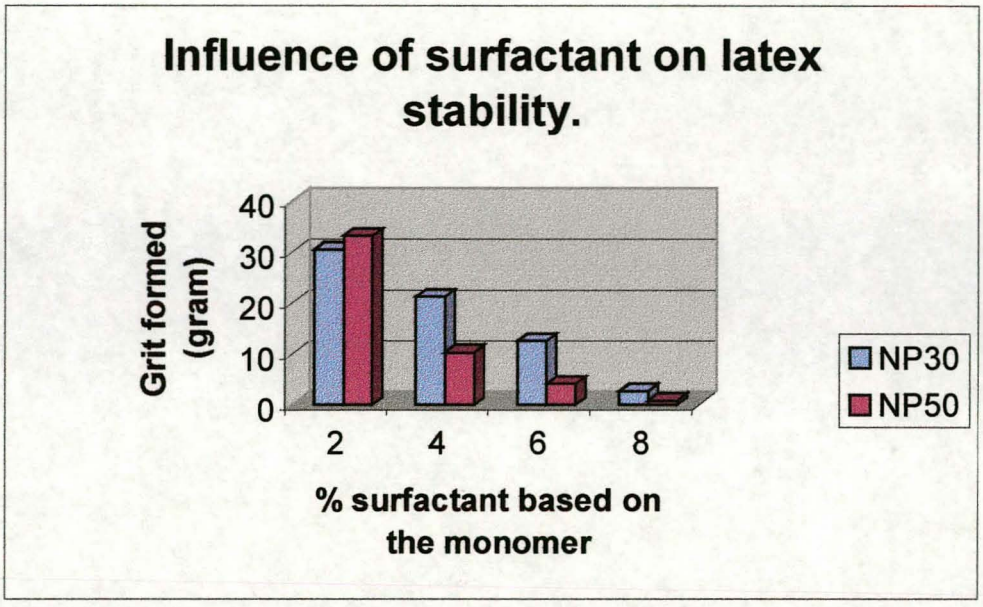

Chart 3.1: Influence of the surfactant on the stability of the grafted latex.

more stable latex when a surfactant with a high HLB value is used. It is therefore recommended to use surfactants with high HLB values to keep the latex in an emulsion. Levels of 8% and above are recommended. The above surfactants were all ethoxylated nonyl phenols (NP). Anionic surfactants, e.g. sodium laurylsulphate, will be ineffective, because the charged group will simply interfere with the stabilizing capability of the natural proteins that keep the latex in emulsion, and destabilization will occur.

3.3 CONCLUSIONS

1. Batch emulsion polymerization is not a viable method for the grafting of ENR50 with MMA.
2. Delayed addition of monomer or the pre-emulsion technique can be used successfully for the grafting of ENR50 with MMA.
3. The delayed addition of monomer technique led to a grafted material with a lower T_g and therefore a material that can be used at lower temperature.
4. The pre-emulsion technique may not lead to a grafted material with a significantly lower T_g, but it led to a material with a higher tan delta peak height value and it will therefore have higher dampening properties.
5. Surfactant levels of 8% or more are needed to keep the latex stabilized.
6. Surfactants with a high HLB value (NP50) show less grit formation and are better than low HLB value surfactants (NP30) for the grafting of ENR50 with MMA.

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CHAPTER 4

DETERMINATION OF THE COMPATIBILITY OF EPOXIDIZED NATURAL RUBBER WITH POLYMETHYL METHACRYLATE AND POLYSTYRENE

4.1 INTRODUCTION

Thermoplastic polymers may be divided into broad classes depending on the type, their chemical composition or behavior. For example they may be classified as crystalline or amorphous polymers, or may be grouped according to whether they are tough or brittle materials. The latter classification has great commercial significance since many amorphous or glassy polymers are brittle and consequently have limited applications.

It has been found that the dispersion of a rubbery polymer in a glassy polymer matrix often results in a significant increase in the impact strength of the glassy polymer, without the corresponding large decrease in modulus and heat distortion temperature that would be obtained through lowering of the glass transition temperature by means of the addition of a plasticizer.

The first commercial polyblend, an impact-resistant polystyrene containing 5% weight of poly (butadiene co-styrene), was introduced by Dow Corning in 1948 [1]. Today a lot of information is available on the compatibility, properties and performance of polyblend systems. A comprehensive list of patents has been compiled by Rosen [2].

Toughening of a glassy polymer by a rubbery component requires not only a two-phase structure but also a certain degree of compatibility between the phases [2]. More often than not the components of a polyblend have such a low affinity for each other that their fusion product will readily break on relatively gentle handling. A brief discussion on compatibility is presented on the following page [3].

If one considers the process of mixing two pure polymers at constant temperature and pressure to form a true molecular solution, the change in Gibbs free energy (ΔG) for such a process is given by:

$$\Delta G = \Delta H - T\Delta S$$

ΔH = change in enthalpy

ΔS = change in entropy

T = absolute temperature (K)

If ΔG is negative then the solution process is thermodynamically favourable. If positive, the two-phase system is favoured. The change in entropy, ΔS, for a mixing process is always positive since mixing increases the randomness, or disorder, of a system. With the positive absolute temperature it is seen that the entropy contribution to the free energy change, -TΔS, always favours the solution process. The important point is, that, because of their high molecular masses the entropy change which occurs when two polymers are mixed is quite small – orders of magnitude less than that for mixing equivalent masses of low molecular mass liquids. As a result of this small contribution of the entropy term, in order that the overall ΔG is negative, the change in enthalpy must be a very small positive value – essentially zero or negative, for solution to occur. Thus one finds that except in systems where ΔH is large and negative (e.g. where hydrogen bond formation occurs) polymer mixtures generally show incompatibility.

From the definition of polyblends (definition: an intimate mixture of two kinds of polymers, with no covalent bonds between them) one notes that it is not the intention to produce a single-phase system. Historically, the oldest and simplest method involves mechanical blending, where a plastic and a noncrosslinked elastomer are blended either on open rolls or through extruders (Matsuo, 1968) [4]. For optimum performance the rubbery phase must be sufficiently insoluble to resist the formation of a single phase but sufficiently compatible to produce good adhesion at the interface [5]. An optimum dispersion, which to a large extent determines the mechanical properties of a blend, exists for each system.

It is known that during the industrial production of blends extensive shearing takes place. This results in chain scission and the possible formation of copolymers, which act as compatibilizers [6]. Good adhesion between the dispersed and continuous phase, brought about by graft formation between the elastomeric and glassy polymer, results in dramatic improvement in the efficiency of the dispersed phase toughening action [4].

Blending of natural rubber with other polymers is widely practiced for developing new thermoplastic elastomers to meet some specific applications. Most of the widely used thermoplastic materials show marked limitations in their use when toughness and high impact resistance are required [7]. These limitations may be overcome by melt mixing these materials with a rubber polymer.

Diversification of the properties of thermoplastics may be obtained most inexpensively by blending with a low T_g component. If the latter is a polymer, depending on the degree of compatibility, one obtains a miscible blend with properties intermediate between those of the constituents, or a phase separated system whose properties are an additive combination of the properties of its components [8]. The latter system is by no means of lesser importance as long as there is good adhesion between phases, e.g. in grafted polymer systems. In fact, certain properties (e.g. impact strength) may best be obtained with heterogeneous blends [9]. As mentioned, ensuring strong chemical or physical bonding between the matrix and the encapsulated rubbery inclusions optimizes these properties.

Epoxidized natural rubber is classed as a modified form of natural rubber with high application potential as an oil-resistant, air-impermeable and high-damping rubber [10, 11]. It has been reported [12, 13] that blends of rigid polyvinylchloride with epoxidized natural rubber, having 50 mol % epoxidization level, form mutually miscible systems. These melt mixed blends have been reported to exhibit a single glass-rubber transition temperature (T_g) lying between that of PVC and ENR. Miscibility was attributed to molecular interactions, such as a donor-acceptor type of a weakly acidic hydrogen, or dipole-dipole interaction.

Epoxidized natural rubber has some unique chemical properties e.g. it has a very reactive epoxy site that can be used in further reactions. It was therefore decided to look at the compatibility of different types of ENR with PMMA and PS and their influence on

the T_g and tan delta (δ) of ENR. The properties of ENR blended with other polymers can be appreciably different, depending on the composition of the former.

4.2 EXPERIMENTAL

4.2.1 Aim

The aim of the experiments was to determine the compatibility of PMMA and PS with different grades of ENR as well as the influence of these polymers on the T_g of the ENR.

4.2.2 Materials

The polymer blends were synthesized by mixing commercially available polymethyl methacrylate and polystyrene with different grades of epoxidized natural rubber (see Table 4.1). The grades of epoxidized natural rubber were all supplied by Kumpulan Guthrie Berhad (Malaysia).

4.2.3 Blending procedure

The blending of PMMA and PS with the different grades of ENR was performed at a temperature of 160 °C in a Brabender Plasticorder, fitted with an oil-heated twin-roll mill. A shear rate of 30 r.p.m. was used in most instances. Shear forces influence the heat build-up in the polymer and the bath temperature was varied to achieve the desired final melt temperature. At the start the PMMA or PS was allowed to melt for one minute, and ENR, in solid form, was added thereafter. The total mixing time of ENR with PMMA or PS was 6 minutes in all cases. The molten mix was then sheeted out in the tight nip of a laboratory two-roll mill. The sheeted-out stock was pressed between two polished aluminium platens and left to cool. The PMMA and PS were blended on a weight percentage of 20% with the different grades of ENR. In the case of ENR50, PMMA was also added in 40% as well as 50% weight to the ENR.

Dynamic mechanical properties were measured using a Polymer Laboratories dynamic mechanical analyzer at a frequency of 1Hz. The samples were run from -75 to 150 °C and data was collected during the heating period. The temperature rise was 5 °C per minute.

Table 4.1: Epoxidized natural rubber used in the blending process.

Materials	Material Abbreviations
Epoxidized natural rubber (25 % mol epoxy groups)	ENR25
Epoxidized natural rubber (50 % mol epoxy groups)	ENR50
Thermoplastic epoxidized natural rubber	TPENR

4.3 RESULTS AND DISCUSSION

The tan delta vs. temperature plots for the different grades of ENR, PMMA and PS can be seen in Appendix 1. The plots for the different grades of ENR and their blends with 20%, 40% and 50% PMMA and 20% PS can also be seen in Appendix 1.

The glass transition temperature (T_g) obtained from the tan delta vs. temperature plots are shown in Table 4.2. The T_g was taken where the storage modulus curve started to drop.

The ENR50 samples with 25% and 50% epoxidization had T_g values of -20.8 and -3 °C respectively, which agree well with the accepted norm that increasing epoxidization increases the T_g value.

The ENR25/PMMA 20% and the ENR25/PS 20% samples both show a sharp decrease in their T_g-1 from -20.8 °C to about -35 °C. Their T_g-2 values correspond well to that of the homopolymer. These samples are incompatible and the lower T_g-1 values can be a result of phase separation of the low-epoxidized natural rubber parts and the high-epoxidized parts of the ENR. The reason behind this phase separation may be the non-random epoxidization of natural rubber to form ENR.

The ENR50/PMMA 20%, ENR50/PMMA 40%, and the ENR50/PS 20 % samples are incompatible and show very little change in their recorded T_g-1 values (about 14 °C). These T_g-1 values are substantially lower than the value of the homopolymer (-3 °C). Again this can be a result of phase separation of the low-epoxidized natural rubber parts

Table 4.2: Glass Transition Temperatures of the different grades of ENR blended with PMMA and PS and their homopolymers (1 Hz).

		T_g (°C)		
Polymer	Appearance	Homopolymer	1	2
ENR25	Rubber	-20.8		
ENR50	Rubber	-3		
TPENR	Rubber	-18.3		
PMMA	Plastic	104.8		
PS	Plastic	110.9		
Blend				
ENR25/PMMA 20%	Plastic		-34.6	106.5
ENR25/PS 20%	Plastic		-35.7	111.7
Blend				
ENR50/PMMA 20%	Plastic		-15.0	103.4
ENR50/PMMA 40%	Plastic		-14.4	103.4
ENR50/PMMA 50%	Rubber		-0.3	121.3
ENR50/PS 20%	Plastic		-12.7	111.8
Blend				
TPENR/PMMA 20%	Plastic		-12.2	96.0
TPENR/PS 20%	Plastic		-5.5	99.1

and the high-epoxidized parts of the ENR. ENR50/PMMA 50% is the only sample that shows a higher T_g-1 (-0.3 °C) than the homopolymer (-3 °C). This is an indication that blending is beginning to take place at this increased level of PMMA loading.

The T_g-1 values of the TPENR/PMMA 20% and the TPENR/PS samples increased from that of the homopolymer (-18 °C) to -12 °C and -5 °C, respectively. Their T_g-2 values also decreased from that of the homopolymer (111 °C) to 96 °C and 99 °C, respectively. Because of this upward and downward shift of the glass transition temperatures, they show the best compatibility.

Of the samples tested, TPENR showed the best compatibility with PMMA and PS, but because low temperature impact capability was more important than this compatibility capability of the rubber, ENR25 was the best rubber to continue further experimentation

with. ENR25 was not commercially available during the experimental phase and it was therefore decided to, nonetheless, continue experimental work with ENR50.

4.4 CONCLUSIONS

1. ENR25 shows a decrease in T_g when 20% PMMA and 20% PS are respectively blended with it.
2. ENR25 is incompatible with 20% PMMA and with 20% PS.
3. ENR50 shows a decrease in T_g when 20% PMMA, 40% PMMA and 20% PS are respectively blended with it.
4. ENR50 is incompatible with 20% PMMA, 40% PMMA and with 20% PS.
5. ENR50 shows an increase in T_g when 50% PMMA is blended with it. This is an indication that blending is beginning to take place at this higher PMMA loading.
6. TPENR shows an increase in T_g when 20% PMMA and 20% PS are respectively blended with it.
7. TPENR shows the higherst level of compatibility.
8. ENR25 has the lowest T_g (-20.8 °C) and would therefore be the best to use for low temperature impact studies.

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CHAPTER 5

INVESTIGATION INTO THE INFLUENCE OF THE TYPE OF ACID, USED AS GRAFT SITE INITIATOR, ON THE COMPATIBILITY OF ENR50 WITH PMMA

5.1 INTRODUCTION

A graft copolymer consisting of epoxidized natural rubber (ENR50) and methyl methacrylate (MMA) was formed by an emulsion polymerization technique (pre-emulsion). ENR50, in latex form, was used as seed latex. MMA and an acid were then polymerized in the presence of this seed latex. The acid used to create the graft site was either acrylic acid (AA) or methacrylic acid (MAA). See Figure 1.2 in Chapter 1. The two polymer systems, which consist of ungrafted ENR50, grafted ENR50 and phase-separated grafted PMMA exhibit varying degrees of phase separation depending on the type of acid used for graft site formation.

5.2 EXPERIMENTAL

5.2.1 Aim

To investigate the influence of AA or MAA on the system (see Table 5.4) formed when MMA reacts with ENR50.

5.2.2 Materials

The polymer systems were synthesized using commercially available monomers (see Table 5.1). The monomers were used as supplied. The ENR50 was filtered through cheesecloth to get rid of any grit that might be present.

The experimental details of the synthetic procedure and the preparation of cast films are described.

5.2.3 Synthetic procedure for the grafting of ENR50 with MMA

A pre-emulsion of distilled deionized water (DDI), surfactant (NP50), and the relevant monomers was made. The formulations used for the grafting of ENR50 with MMA are given in Table 5.2 and Table 5.3. The pre-emulsion was made by adding ENR50, DDI and NP50 in a 100 ml three-neck reactor and to then stir it. During the stirring process MMA and AA or MAA were added.

In a 500 ml four-necked reactor, 14 g deionized and de-aerated water was stirred and gently warmed while purging the system with nitrogen. The nitrogen blanket was maintained throughout. At 82 °C, 25% of the potassium persulphate solution (2% based on the monomer weight) and 2% of the monomer solution, were added and the reaction allowed to proceed at 82 °C for 15 minutes. The remainder of the monomer emulsion and initiator solution were introduced over a 3.5-4 hour period, while maintaining the reaction temperature at 82 °C. The reaction mixture was then heated to 85 °C for 30 minutes. On completion of the reaction, it was cooled to below 30 °C, the pH was adjusted to 7.0 with concentrated NaOH and the crude product filtered through cheesecloth. A stirring speed of 250 revolutions per minute was used throughout.

5.2.4 Preparation of grafted latex for film casting

An aluminum pan was filled with latex and allowed to dry at room temperature (23 °C).

A Perkin-Elmer DMA 7e dynamic mechanical analyzer was employed for the dynamic mechanical measurements. The temperature range studied was from -60 °C to 160 °C. The heating rate was 5 °C / min and the frequency employed was 1 Hz.

Table 5.1: Monomers and reagents used in the synthesis of the grafted ENR50.

Materials	Material Abbreviations	Supplier
Epoxidized natural rubber (50 % mol epoxy groups)	ENR50	Kumpulan Guthrie Berhad (Malaysia)
Methyl methacrylate	MMA	Plascon
Acrylic / Methacrylic acid	AA / MAA	Saarchem / Plascon
Potassium persulphate	KPA	UniLab
Nonyl phenol50 (Surfactant)	NP50	Saarchem

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	49
AA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	=====	=====	
	106.41	38.5	

Table 5.2: Formulation used for the reaction of ENR50 with MMA, with the use of AA as a graft site.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	49
MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	=====	=====	
	106.41	38.5	

Table 5.3: Formulation used for the reaction of ENR50 with MMA, with the use of MAA as a graft site.

5.3 RESULTS AND DISCUSSION

Emulsion polymerization products, formed in the presence of seed latex, show complex morphologies according to the literature [1], i.e. a salami structure with occlusions of polymer in a rubber phase and probably including core-shell.

The tan δ vs. temperature plots for ENR50 grafted by MMA through graft site formation by AA and MAA are shown in Figures 5.1 and 5.2.

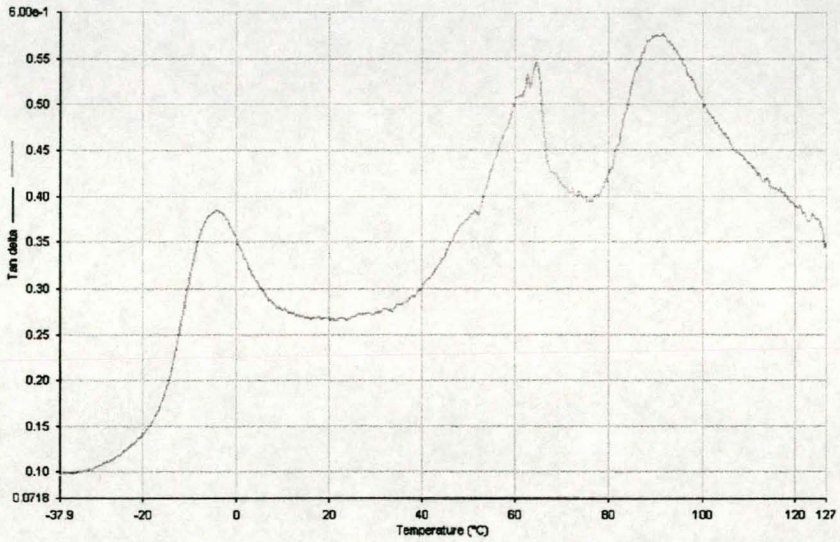

Figure 5.1: Tan δ vs. temperature curve for system A (ENR50/MMA/AA) at 1 Hz.

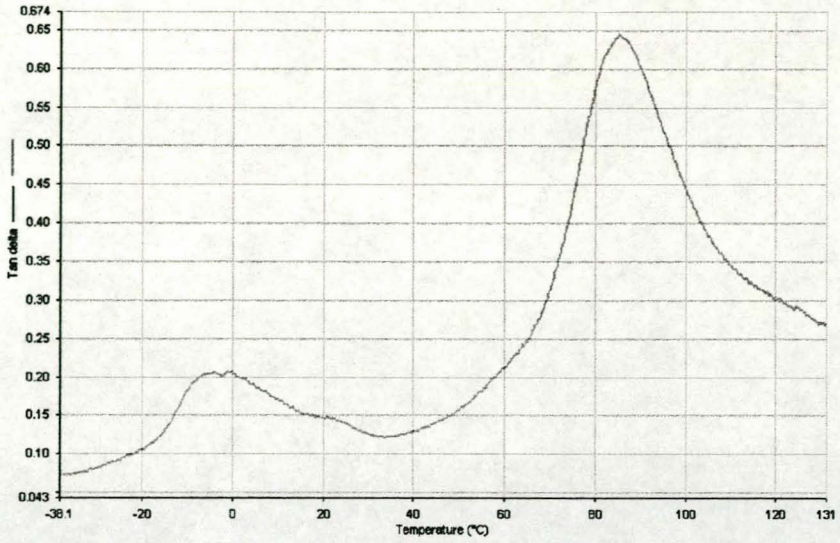

Figure 5.2: Tan δ vs. temperature curve for system B (ENR50/MMA/MAA) at 1 Hz.

The glass transition temperatures (T_g) of the homopolymer, ungrafted rubber and grafted rubber are obtained from the storage modulus (E') vs. temperature plots and are shown in Table 5.4.

Table 5.4: Glass Transition Temperatures of the Polymer Systems and their homopolymers (1 Hz).

	T_g (°C)		
Polymer	Homopolymer	Ungrafted rubber	Grafted rubber
ENR50	-5.1		
PMMA	106		
System A, ENR50/MMA/AA		-14.5	63.6
System B, ENR50/MMA/MAA		-13	49

Both systems, namely A and B, show two well-defined tan δ peaks. In both cases an intermediary stage is also clearly defined. This is an indication that mixing between the ENR50 and PMMA took place. In both cases the position of the first and second peaks, in comparison to their homopolymer positions, are shifted to lower temperatures. Although the lower temperature shift in the first peak (ENR50) is relatively small, a substantial lower shift in temperature is seen for the second peak. In system B, where MAA is used, the downward shift of the second peak is even higher. The inward shifting of the peaks in polymer-polymer blends has been shown by many workers to be an indication of molecular mixing [1-5]. Accordingly, it could be said that in system A, mixing is taking place, while for system B, even more mixing occurs. The shift in the T_g to 63 °C with the AA graft site and 49 °C with the MAA graft site indicates the ratios of ENR50 / PMMA of 0.5 and 0.49 respectively, as determined by the equation:

$$T_{gblend} = \nu_{ENR} T_{gENR} + \nu_{PMMA} T_{gPMMA} \quad (\nu = \text{volume fraction})$$

The dynamic loss modulus (E") vs. temperature plots for systems A and B are shown in Figures 5.3 and 5.4. The polymer system A shows one poorly defined low temperature peak and one well-defined high temperature peak that is broadened appreciably into a shoulder by phase separated PMMA. It will be shown later (Chapter 9) that in order to have a better low temperature impact resistance, the area of the low temperature E" peak should be large. This is not the case in Figure 5.3 as it is in Figure 5.4.

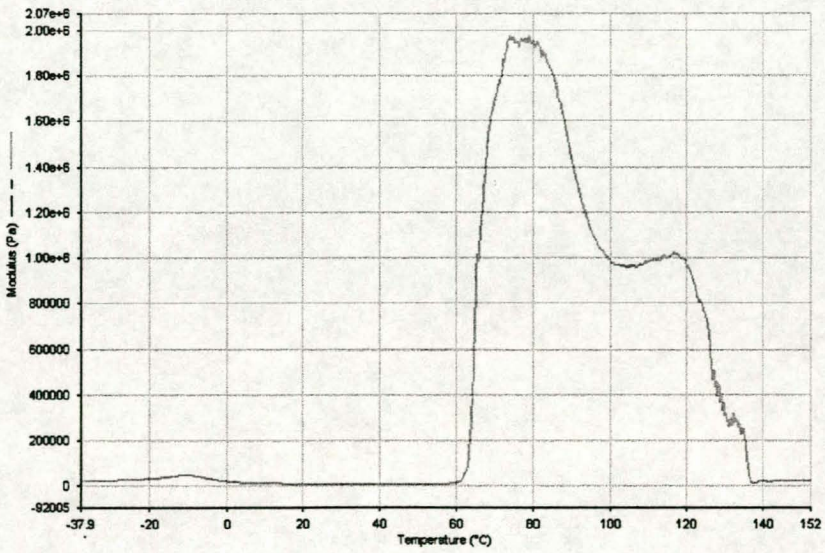

Figure 5.3: Loss modulus (E") vs. temperature curve for system A (ENR50/MMA/AA) at 1 Hz.

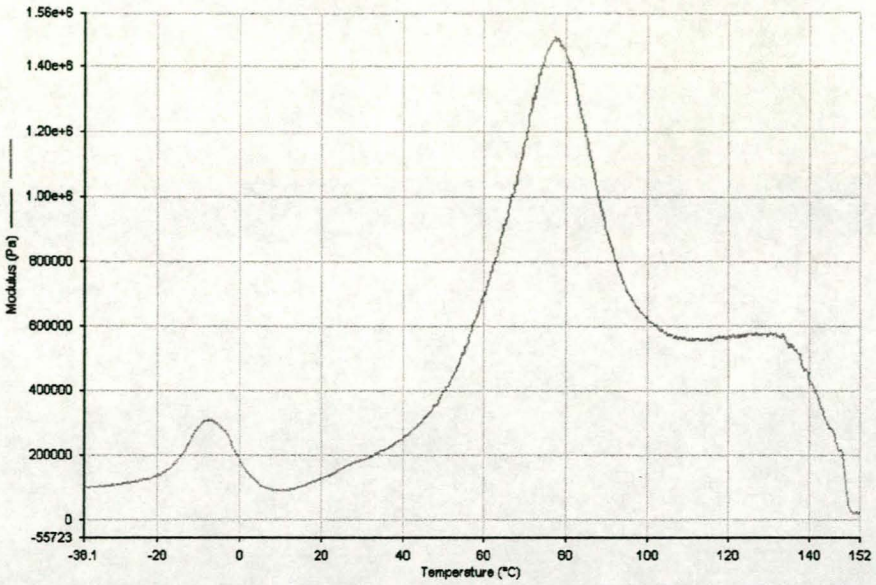

Figure 5.4: Loss modulus (E") vs. temperature curve for system B (ENR50/MMA/MAA) at 1 Hz.

In Section 7.2.4.4 of Chapter 7 the GPEC result of the grafted rubber shows no homopolymer formation. In paragraph 7.2.3.6 of Chapter 7 the DEA result shows hardly any polarity in the rubber peak. In Figure 5.4 the E" curve shows a fair sized rubber peak (from -20 to 10 °C). This indicates the presence of non-random epoxidized rubber that does not graft, as shown in the GPEC results. The lower T_g of the rubber, compared to that of ENR50, shows that the rubber having fewer epoxy groups phase separated from the rubber having a higher epoxidization. This is expected as rubber epoxidization is a heterogeneous process on latex particles (see section 2.4.1). The higher epoxy rubber fraction would also be more prone to grafting by MMA, leading to a further incentive for separation.

The shoulder (after 100 °C) on the right of the mixed blend in the E" curve of Figure 5.4 is phase-separated grafted-PMMA. The degree and amount of phase separation is small and the domains of grafted-PMMA must be very small. Phase separation is only possible here if the chain lengths of the grafted-PMMA are long enough to allow it. Short chains mix as they are known to compatibilize (especially under 10 000-15 000 molar

mass). The T_g of the shoulder can be calculated to give a value of about 100 °C, which correlates to the measured T_g of 106 °C.

5.4 CONCLUSIONS

1. System B (ENR50/MMA/MAA) shows more mixing than system A (ENR50/MMA/AA).
2. The low temperature loss modulus peak of system B shows more low temperature impact potential than system A.
3. Non-random epoxidized rubber is present in the ENR. This is indicated by the loss modulus peak of system B where a rubber peak is present, that does not graft, as shown in the GPEC results of paragraph 7.2.4.4 in Chapter 7.
4. Phase-separated grafted-PMMA is present as shown by the loss moduli curves.
5. The areas under the loss moduli curves can be used for quantitative work, whereas the tan delta curves can be used for qualitative work, because the interaction of the two pure homopolymer phases indicates the degree of mixing.
6. Many workers [6-9] have cited core-shell models for two-stage emulsion systems, where the first is a seed. The results in this study could also point to such a system.

From the results in this study (points 1 and 2 of the conclusions) it was decided to work with MAA in further reactions.

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CHAPTER 6

THE CHARACTERIZATION OF ENR50 BY DYNAMIC MECHANICAL AND DIELECTRIC ANALYTICAL TECHNIQUES

6.1 INTRODUCTION

Dynamic mechanical analysis (DMA) and dielectric analysis (DEA) are becoming increasingly useful techniques for the characterization of polymers and viscoelastic properties. As polymers become increasingly popular and replace traditional materials in many applications, the information provided by these techniques is very useful to those in research and development, quality assurance and quality control, failure analysis and process control [1].

Dynamic mechanical analysis (DMA) is the study of the movement of polymer chains by the application of a sinusoidally varying total force programmed in milliNewton (mN) onto the polymer [2]. The total force applied to the polymer is the sum of the static force and dynamic force with a chosen frequency in Hertz (Hz). The sample responds to the applied force with an oscillating amplitude, measured in micrometers (μm). The displacement amplitude corresponds to the average energy recovered in one cycle of oscillation in an elastic deformation. The sample also responds to the applied force with a phase lag (δ), reported in degrees (°). The phase lag corresponds to the average energy lost in one cycle of oscillation in a viscous deformation. Elastic and damping properties are calculated using fundamental relationships such as Hooke's law and Newton's law. From the amplitude the storage modulus (E'), and from the phase lag the loss modulus (E"), are determined. The tan δ is the ratio of E" to E'. A schematic representation of the operation of the DMA is shown in Figure 6.1.

Dielectric analysis (DEA) is the study of the mobility of charged sites in a material [3]. These charged sites are typically ions or dipoles. The mobility of the dipoles and ions are measured by applying a sinusoidal voltage to the sample and measuring the current. Dipoles in the material will attempt to orientate in the electrical field that is generated, while the ions will move to the electrode of opposite polarity. See Figure 6.2.

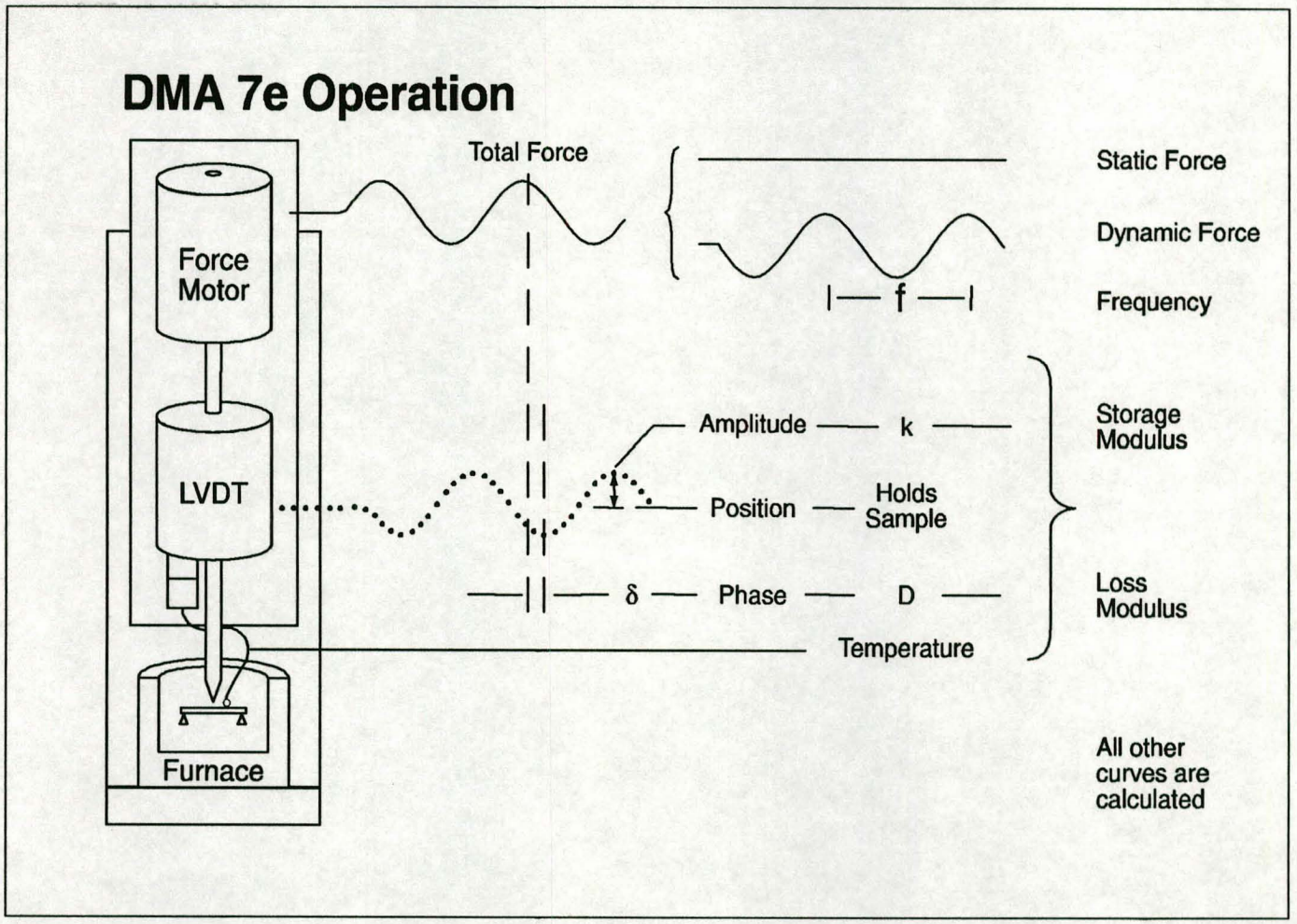

Figure 6.1: Schematic diagram of the operation of the DMA 7e.

The measured current can be resolved into two fundamental dielectric characteristics: capacitance and conductance.

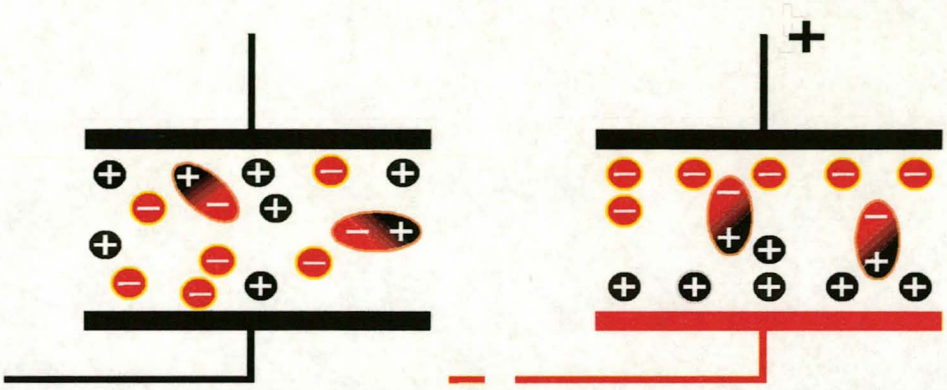

Figure 6.2: Representation of the orientation of dipoles and the movement of ions between the DEA electrodes [4].

The Micromet Instruments Eumetric System III Microdielectrometer is used to apply the sinusoidal voltage to the bottom plate of the Perkin Elmer Dynamic Mechanical Analyzer 7e. The signal goes through the sample, top plate, and core rod and into the Micromet Mid-Conductivity interface box. See Figure 6.3. The sample tube is shielded to enhance the signal [4].

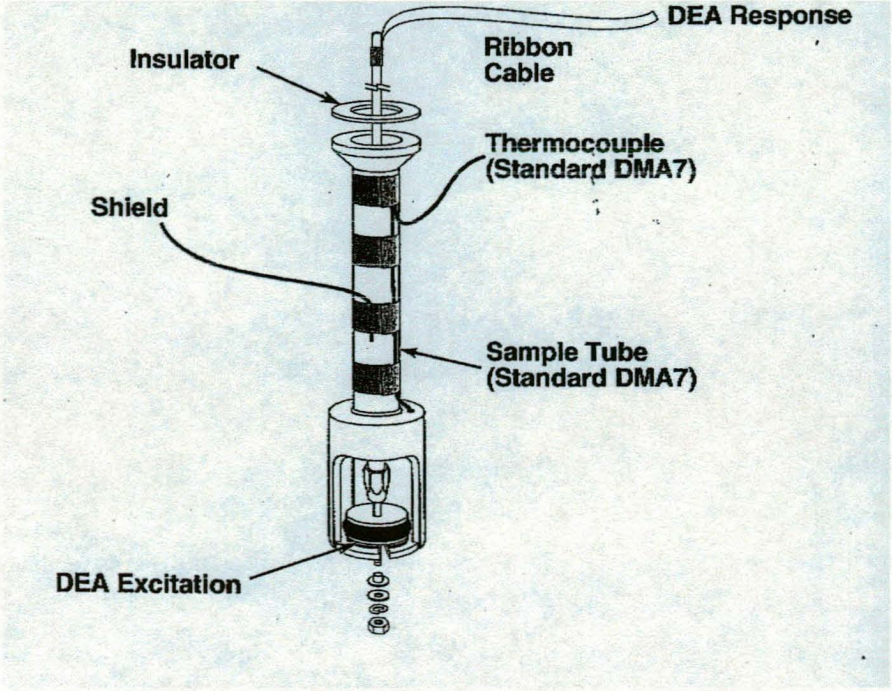

Figure 6.3: DMA-DEA measuring system [4].

In dielectric measurements two items are very important: the A/D ratio and the base capacitance. The A/D ratio is the ratio of the electrode area (A) to the distance (D) between the electrode. In the experiments, the area of the top plate of the DMA is used, and the distance is the height of the sample. For accurate permittivity results it is also important to account for stray capacitance in the electrode configuration. This capacitance, known as the base capacitance, can be determined experimentally. As mentioned, by comparing the applied voltage to the measured voltage two fundamental electrical characteristics can be determined, namely capacitance and conductance. The capacitance and conductance can be studied as a function of temperature, time and frequency and are used to determine other electrical properties [4].

6.1.1 Definition of terms and relationships [5]

Capacitance is the ability to store electrical charge. It is proportional to the relative permittivity (Є'), which is a measure of the alignment and the number of dipoles in the sample. Capacitance can be determined by the use of the following relationship:

$$C = \frac{I \sin \delta}{V 2\pi f}$$

- C = *capacitance (farads)*
- I = *current (amps)*
- δ = *phase lag of measured voltage to applied voltage (degrees)*
- V = *voltage (volts)*
- f = *frequency (Hz)*

Conductance is the ability to transfer electric charge. Conductance is proportional to the dielectric loss factor (Є"), which is a measure of the energy absorbed and lost in the process of aligning dipoles.

Conductance can be determined by the use of the following relationship:

$$R^{-1} = \frac{I \cos \delta}{V}$$

R^{-1} = *conductance (ohms^{-1})*
I = *current (amps)*
δ = *phase lag (degrees)*
V = *voltage (volts)*

Relative permittivity (ε') is often referred to as the dielectric constant and is used to characterize molecular relaxation. It is proportionate to the capacitance and the A/D ratio. When the voltage is applied, dipoles gradually align with the electric field and the permittivity increases. This change in permittivity is used to identify the dipole relaxations.

The **dielectric loss factor (ε")** is used to characterize molecular relaxations and identify rheological transformations. It can be defined by the following relationship:

$$\varepsilon'' = \varepsilon''_{dipole} + \frac{\sigma}{\omega \varepsilon_0}$$

ε" = *loss factor (dimensionless)*
ε''_{dipole} = *energy lost in aligning dipoles (dimensionless)*
σ = *bulk ionic conductivity (ohm-centimeters^{-1})*
ω = *angular frequency (2πf) (rad / sec)*
ε_0 = *permittivity of free space (farads / meter)*

Combining these two techniques [4] allows incremental information to be obtained about the behaviour of polymer systems. The use of the combination of DMA and DEA for the characterization of polymers is quite new. Simultaneous DMA-DEA measurements are achieved by using the DMA parallel plate, or cup and plate measuring system, simultaneously, as electrodes for the DEA. See Figure 6.4.

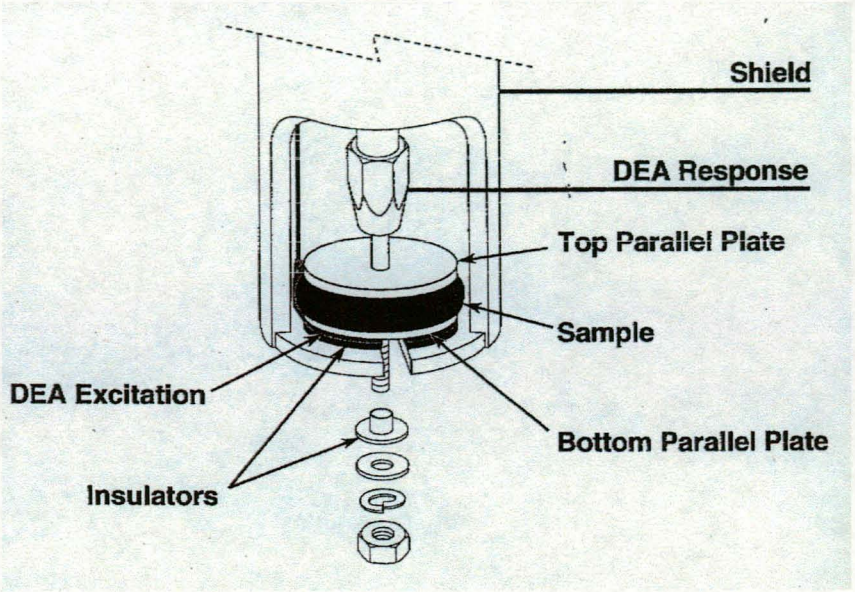

Figure 6.4: Schematic representation of DEA coupled to the DMA parallel plate [4].

6.2 EXPERIMENTAL

6.2.1 Aim

To investigate the usefulness of using the simultaneous configuration of the DMA with the DEA for the analysis of ENR50.

6.2.2 Materials and sample preparation

Kumpulan Guthrie Berhad (Malaysia) kindly supplied the ENR50 sample analyzed. The ENR50 used was first poured through cheesecloth to retrieve any grit. It was then cast

into an aluminium pan to form a latex film. The film was cut into pieces suitable for analysis by a sharp razor blade with the edges lubricated with water.

6.2.3 Procedure used for the analyses

The cup and plate measuring system was mounted on the Perkin-Elmer DMA 7e equipped with the DEA interface kit. The probe weight was tared and the height zeroed. The Time/Temperature mode and the parallel plate measuring system were selected, using the Perkin-Elmer Pyris software as shown in Table 6.1.

Table 6.1: Parameters used in simultaneous DMA/DEA analyses.

Sample	Grafted ENR50	Disk
Instrumental	DMA	Perkin-Elmer DMA 7e with the DEA kit
	Measuring System	15 mm Cup and plate
	Geometry	Disk
Environmental	Purge	Nitrogen, (30 cc/min)
	Coolant	Liquid Nitrogen
Parameters	Mode	Temperature Scan
	Temperature Program	-60 to 160 °C at 5 C/min
	Static Force	Amplitude Control
	Dynamic Force	Amplitude Control
	Amplitude	8 µm
	Frequency	1.00 Hz
Instrumental	DEA	Micromet Eumetric System III Microdielecrometer
	Interface	Mid Conductivity
Parameters	Sensor	Mono/User
	A/D ratio	7.1 cm
	Base Capacitance	20 pF
	Frequencies	1, 10, 50, 1000, 10000, 100000 Hz
	Cycle Time	15 seconds
	Duration	45 minutes

Amplitude control of 8 µm was used and a frequency of 1 Hz was selected. The furnace was raised and the temperature programmed to go to -60 °C. The run was then programmed to go to 160 °C at 5 °C/min.

The Micromet Instruments Eumetric System III microdielectrometer was connected to the Perkin-Elmer DEA interface kit. The DEA parameters were selected using the Micromet Software package. The A/D ratio was calculated to be 7,1 cm and the base capacitance 20 picofarads. The DEA data was collected at frequencies 1, 10, 50,1000, 10000 and 100000 Hz. The sample was mounted between the cup and plate. The sample was allowed to reach the temperature of -60 °C and was equilibrated until constant amplitude was achieved. A new height was then read and the DMA 7e and DEA were started simultaneously.

It was thought suitable to study the effect of a high shear force on the ENR50 to see if fragmentation occurred as well as to show how powerful simultaneous DMA-DEA analysis is. A SILVERSON LR4 supplied the shear force. The shear force was applied onto the ENR50 latex for 5, 10 and 60 minutes at a time.

This effect was not just studied by DMA-DEA, but also by atomic force microscopy. The atomic force microscope used was a TMX 2000 Explorer (Topometrix).

6.3 RESULTS AND DISCUSSION

The simultaneous DMA-DEA results are shown in Figures 6.5 and 6.6. From the results of DMA 7e (Figure 6.5) an increase in onset temperature of tan delta (T_g), as well as a decrease in tan delta peak height (dampening), is seen as we increase the shear time. This may be due to crosslinking of the ENR50. From the DEA results (Figure 6.6) a decrease in onset temperature of log permittivity is observed. Two definite peaks can also be seen. Therefore we can conclude that some chains must have been broken and that fractions with higher chain mobility were produced than before the experiment. The broken fragments have a high polarity, as they do not show up in the DMA 7e. The fragments are probably hydroxyl terminated molecules. Therefore, under the right shear conditions one may lose some degree of dampening, but gain low temperature capability as well as hydroxyl terminated molecules that may help with binder bonding.

DMA

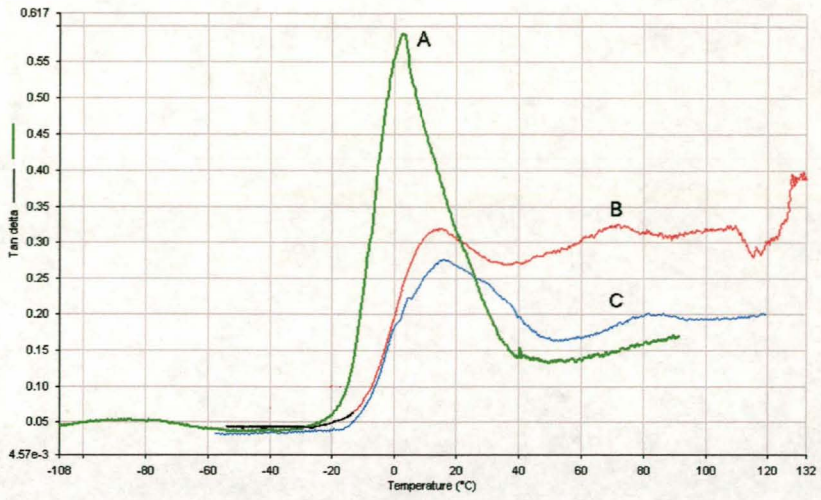

Figure 6.5: Effect of shear force on T_g and tan delta peak values. (A) ENR50, (B) shear applied for 10 minutes and (C) shear applied for 60 minutes.

DEA

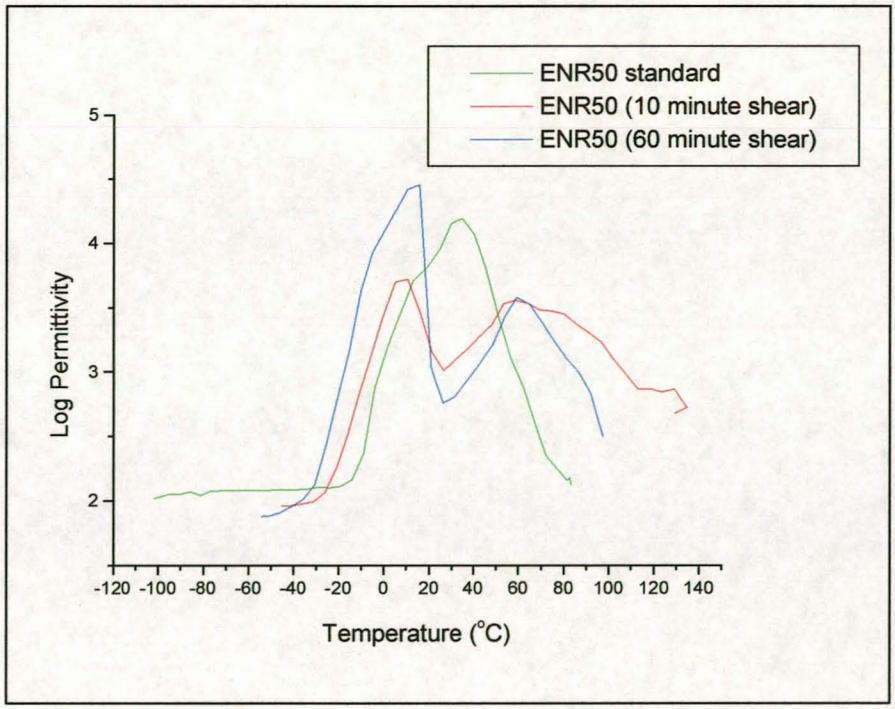

Figure 6.6: Effect of shear force on the permittivity of ENR50.

The results of atomic force microscopy can be seen in Figures 6.8 to 6.11. The roughness values (calculated from Figures 6.8 to 6.11) against the time of shear are shown in Figure 6.7.

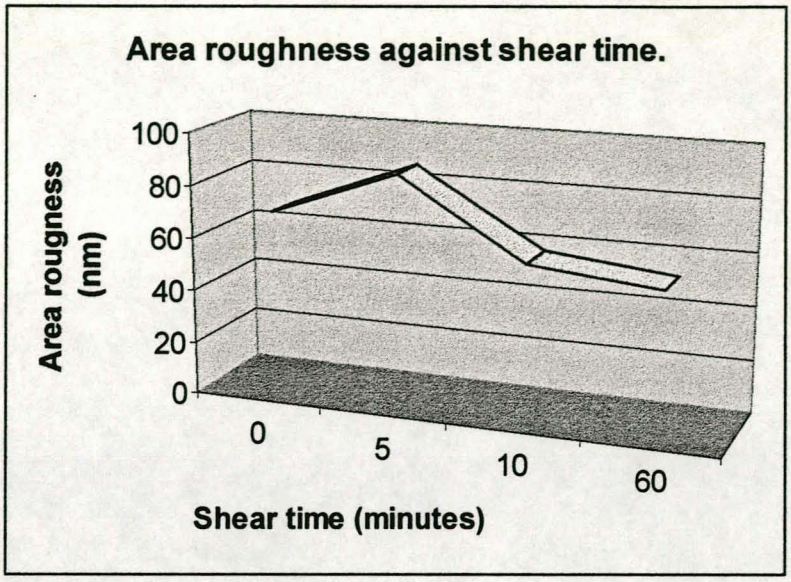

Figure 6.7: Area roughness of cast ENR50 film against shear time.

As can be seen, the roughness value increases sharply after 5 minutes. This may be due to initial aggregation. Then it gradually decreases to below that of ENR50. As the shear time increases, the ENR50 film therefore becomes smoother. This may be an indication of smaller particles that are now packed closer together to form the smoother surface.

6.4 CONCLUSIONS

1. The simultaneous configuration of the DMA with the DEA can be used successfully for the analysis of ENR50.
2. ENR50 chains are broken by an increase in shear time, as indicated by two peaks and the decrease in onset temperature of the log permittivity of the DEA peaks in Figure 6.6.
3. Atomic force microscopy can be used successfully to track the decrease in particle-size of the ENR50 latex.

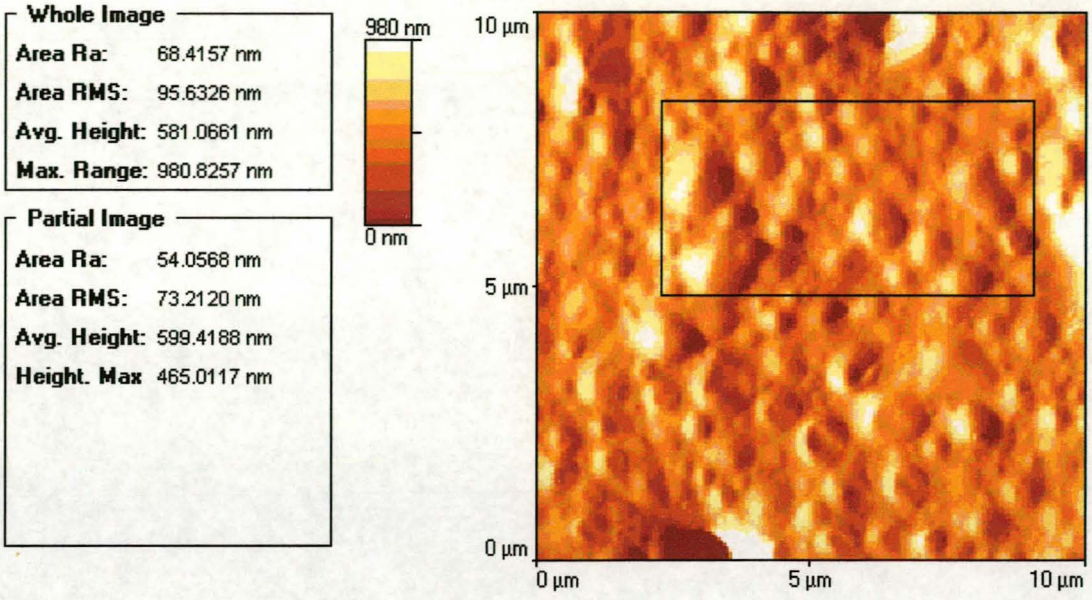

Figure 6.8: Roughness values of ENR50 without shear applied.

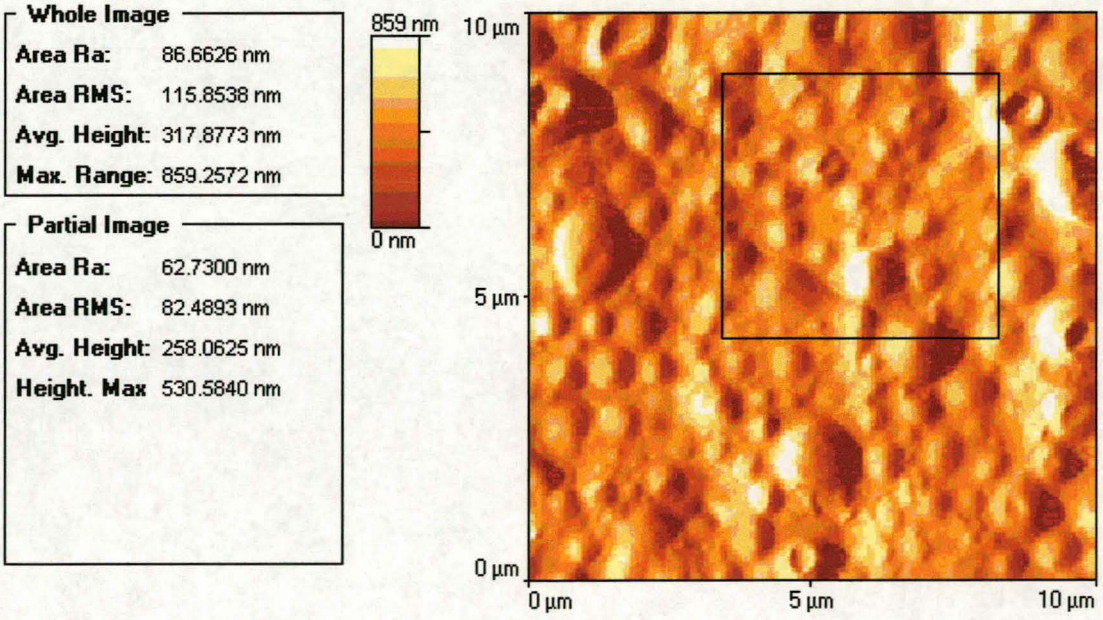

Figure 6.9: Roughness values of ENR50 with 5 minutes of shear applied.

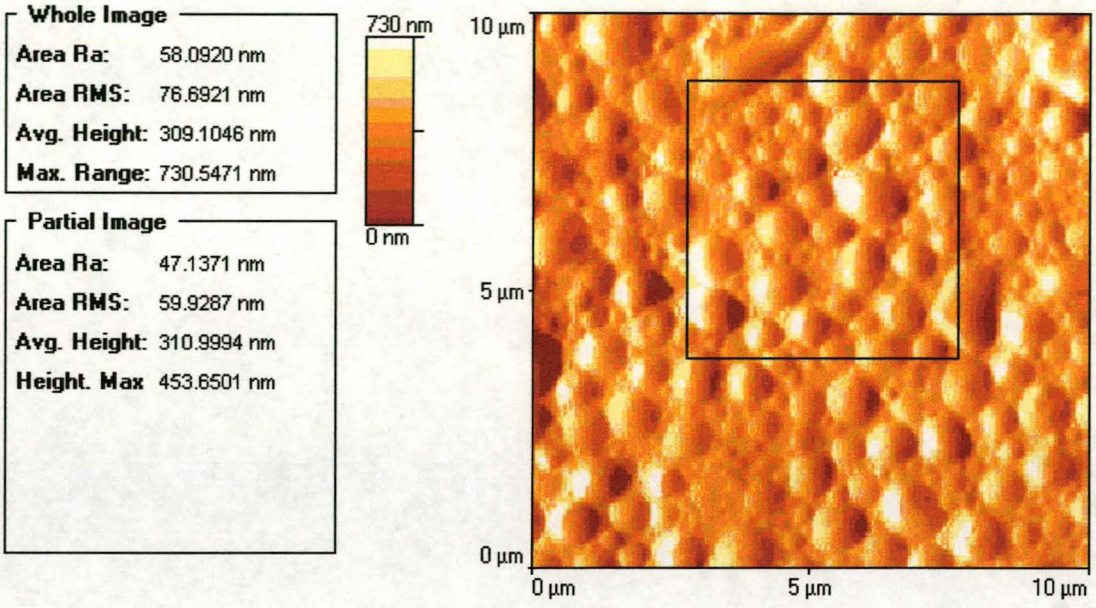

Figure 6.10: Roughness values of ENR50 with 10 minutes of shear applied.

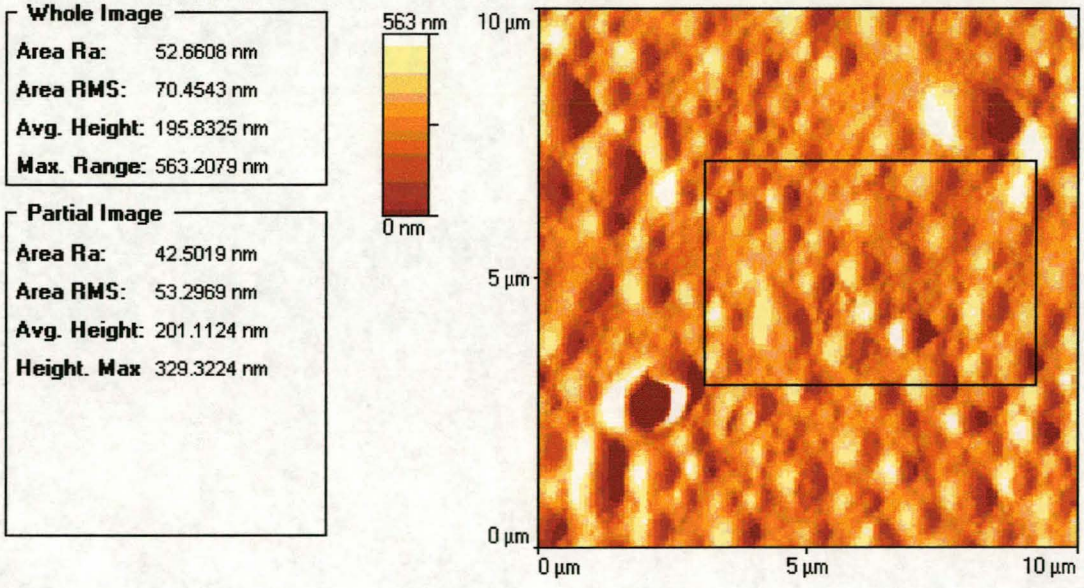

Figure 6.11: Roughness values of ENR50 with 60 minutes of shear applied.

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CHAPTER 7

GRAFTING OF EPOXIDIZED NATURAL RUBBER

7.1 INTRODUCTION

7.1.1 Graft copolymers

A graft copolymer is a polymer comprising molecules with one or more species of block connected to the main chain as side chains, having constitutional or configurational features that differ from those in the main chain, exclusive of branch points [1]. In a graft copolymer, the distinguishing feature of the side chains is constitutional, i.e.; the side chains comprise units derived from at least one species of monomer different from those that supply the units of the main chain [2]. The simplest case of a graft copolymer can be represented by Figure 7.1.

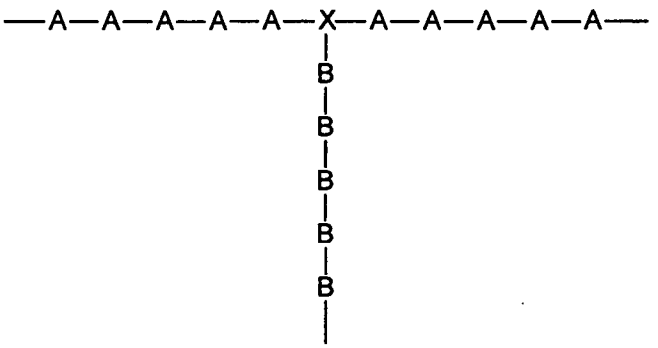


Figure 7.1: Simplest case of a graft copolymer.

where a sequence of A monomer units are referred to as the main chain or backbone, the sequence of B units is the side chain or graft, and X is the unit in the backbone to which the graft is attached. In graft copolymers the backbone and side chains may both be homopolymeric, the backbone may be homopolymeric and the side chains copolymeric or vice versa, or both backbone and side chains may be copolymeric but of

different chemical compositions. Branching in one or more stages and cross-linking may also occur. Cross-linked structures usually cannot be fully characterized because they are insoluble and frequently infusible.

Graft polymerization is a common method for modifying polymer properties [3, 4]. Because the main chain and the branch chain are usually thermodynamically incompatible, most graft copolymers can be classified as multiphase polymers in the solid state, analogous to polymer blends, block copolymers, and interpenetrating polymer networks [4]. Since the casting solvent and the nature of its interaction with the polymer blocks can affect the morphology of heterophase polymers, the physical properties are also expected to depend on the casting solvent [5].

Free-radical polymerization methods are the oldest and most widely used procedures for the synthesis of graft polymers, because they are relatively simple [3]. However, they usually give heterogeneous materials that are difficult to characterize. Historically, graft copolymers have been prepared by polymerization of a monomer in the presence of a preformed backbone. The monomer can be polymerized by any of the traditional modes of polymerization. Backbones for free-radical graft copolymerization require the presence of an atom or group that can be abstracted or displaced by another radical, by radiation of sufficient intensity, or by mechanical degradation. Just about any backbone will do. Although free-radical graft copolymerization methods are the simplest, oldest, and most widely used [3], the least specific grafting sites and the most poorly defined branches result. Backbones for ionic or condensation polymerization require a reactive site or functional group capable of participating in specific chemical reactions. The products are well defined and the properties of the branches can be controlled.

Graft copolymers can be prepared by copolymerizing preformed branches with the monomer constituting the major portion of the backbone. The branch must have an end group capable of copolymerizing with the monomer by the mode of polymerization being used. Alternatively, preformed branches can be coupled with a backbone, if it has functional groups that can react with a group on the preformed branch.

7.1.2 Graft copolymers with natural rubber

Among the earliest recorded attempts to modify rubber by polymerization of monomers dissolved in rubber or dispersed in latex were those sponsored by the Rubber Growers' Association and reported to the 1938 Rubber Technology Conference [6]. Although the practicality of modifying rubber by polymerizing vinyl monomers in its presence has therefore been known for some time, the graft-polymer nature of the products has only been established since a study done by Bloomfield and Merrett in 1954.

Graft polymers, as said, result when vinyl monomers are polymerized in the presence of NR, either in solution, in latex or in bulk rubber swollen with monomer, and some of the polymeric chains become attached to the rubber molecules. With a few exceptions, rubber or the impurities contained in it, does not inhibit polymerization of vinyl monomers (conventionally initiated). The notable exceptions are vinyl acetate and vinyl chloride, both of which are severely retarded even by pure polyisoprenes. However, there is a theoretical explanation for this behaviour [7].

When polymerization is conducted in solution, the combination of polymer with rubber occurs only when peroxidic initiators are used and it appears to be essential that the initiator is capable of some direct action on the rubber, since polymerization initiators which have no action on rubber (e.g. azo-bis-isobutyronitrile) give simply a mixture of rubber and vinyl polymer which can be separated by fractional precipitation. This specific catalyst effect precludes a chain-transfer mechanism for the graft polymerization of NR, and all other mechanisms involving prior attack of vinyl polymer radicals on the polyisoprene. The cause of this specific initiator effect, and the mechanism of graft polymerization, have been determined by using ^{14}C-labelled initiators. Benzoyl peroxide initiates graft polymerization by prior reaction of the derived phenyl and benzoyloxy radicals with the polyisoprene by addition to the double bond, and by abstracting α-methylenic hydrogen atoms to give polyisoprenic alkyl and alkenyl radicals, respectively, which act as loci for methyl methacrylate polymerization.

The initiator specificity is less pronounced in polymerizations conducted in latex or in bulk rubber [8]. Under these conditions the proximity of rubber and polymer molecules in a non-mobile system may permit chain transfer or other interactions to occur [9].

Under favourable conditions for graft-polymerization of monomers in rubber latex the polymerization may be made to proceed wholly within the rubber particles, thus avoiding the formation of free polymer particles in the aqueous phase. Electron micrographs of large-particle fractions of *Hevea* latex fail to reveal any of the small polymer particles, which would be expected to result from such aqueous-phase emulsion polymerization of monomer [10].

Because the grafting of polymeric side chains onto rubber depends on the attack of initiator radicals and not vinyl polymer radicals with rubber molecules, there is inevitably competition between monomer and rubber for the available initiator radicals. Since monomer-initiator interaction leads to conventional homopolymerization not involving rubber, the products of graft copolymerization are certain to contain some free homopolymer. Furthermore, even when using high monomer-rubber ratios only a part of the rubber undergoes the grafting reaction. The product of the polymerization reaction is therefore a mixture of free rubber, a graft copolymer and a free vinyl polymer; these mixtures have been given the generic name "Heveaplus". The graft copolymer acts as an "alloying" component, making difficult the separation of the free rubber.

When water-soluble initiators are used in latex-monomer systems much of the graft-polymerization occurs at or near the surface of the latex particles. This results in a higher degree of grafting onto the smaller rubber particles than onto the larger ones [10] and also reduces cohesion of the particle to such an extent that cast films from such latices are non-coherent and break up on drying. With rubber-soluble initiators coherent films are obtained [11]. The latices also behave very differently on coagulation, the former type gives non-coherent crumbs or powders, and the latter type gives rubbery masses.

7.1.3 Graft copolymers with epoxidized natural rubber

No attempt has been made to date, to graft epoxidized natural rubber in latex form with vinyl monomers. Therefore in this work an attempt will be made to graft epoxidized natural rubber with methyl methacrylate and to characterize the success of this grafting process. A novel method will also be used to create a grafted epoxidized natural rubber. Firstly a graft site will be created by the reaction between acrylic or methacrylic acid and

the epoxy group of ENR. This will create a vinyl group for further polymerization reactions. After the creation of this "grafting" site, MMA is to be used for further polymerization.

7.2 EXPERIMENTAL

7.2.1 POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF ENR50

7.2.1.1 Aim

To investigate the particle-size of MMA after the reaction of MMA with ENR50.

7.2.1.2 Materials

The methyl methacrylate and ENR50 were used as supplied. Plascon supplied the MMA and MAA. Saarchem supplied NP100. The ENR50 was filtered through cheesecloth to get rid of any grit that might be present.

7.2.1.3 Synthetic procedure

A pre-emulsion of deionized water (DDI), surfactant (NP100), and the relevant monomers was made. See Table 7.1. ENR50, DDI and NP100 were added in a 100 ml three-neck reactor, while stirring. MMA and MAA were then added consecutively, while stirring vigorously.

In a 500 ml four-necked reactor, 14 g of deionized and de-aerated water was stirred and gently warmed while purging the system with nitrogen. The nitrogen blanket was maintained throughout. At 82 °C, 25 % of the potassium persulphate solution (2% based on the monomer weight) and 2% of the monomer solution were added. The reaction temperature was held at 82 °C for 15 minutes. The remainder of the monomer emulsion and initiator solution was added over a 3.5-4 hour period while maintaining the reaction

temperature at 82 °C. After addition was completed, the temperature was adjusted to 85 °C and held at this temperature for a further 30 minutes. After the completion, the reaction mixture was cooled to below 30 °C. The pH was adjusted to 7.0 with concentrated NaOH and filtered through cheesecloth. During the run the stirring speed was maintained at 250 revolutions per minute. (See Section 5.2.3.)

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	26.125	-	-
NP100 (Surfactant)	2.8	2.8	8
ENR50	47.73	26.25	75
MMA	8.4	8.4	24
MAA	0.35	0.35	1
	85.405	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	=====	=====	
	107.105	38.5	

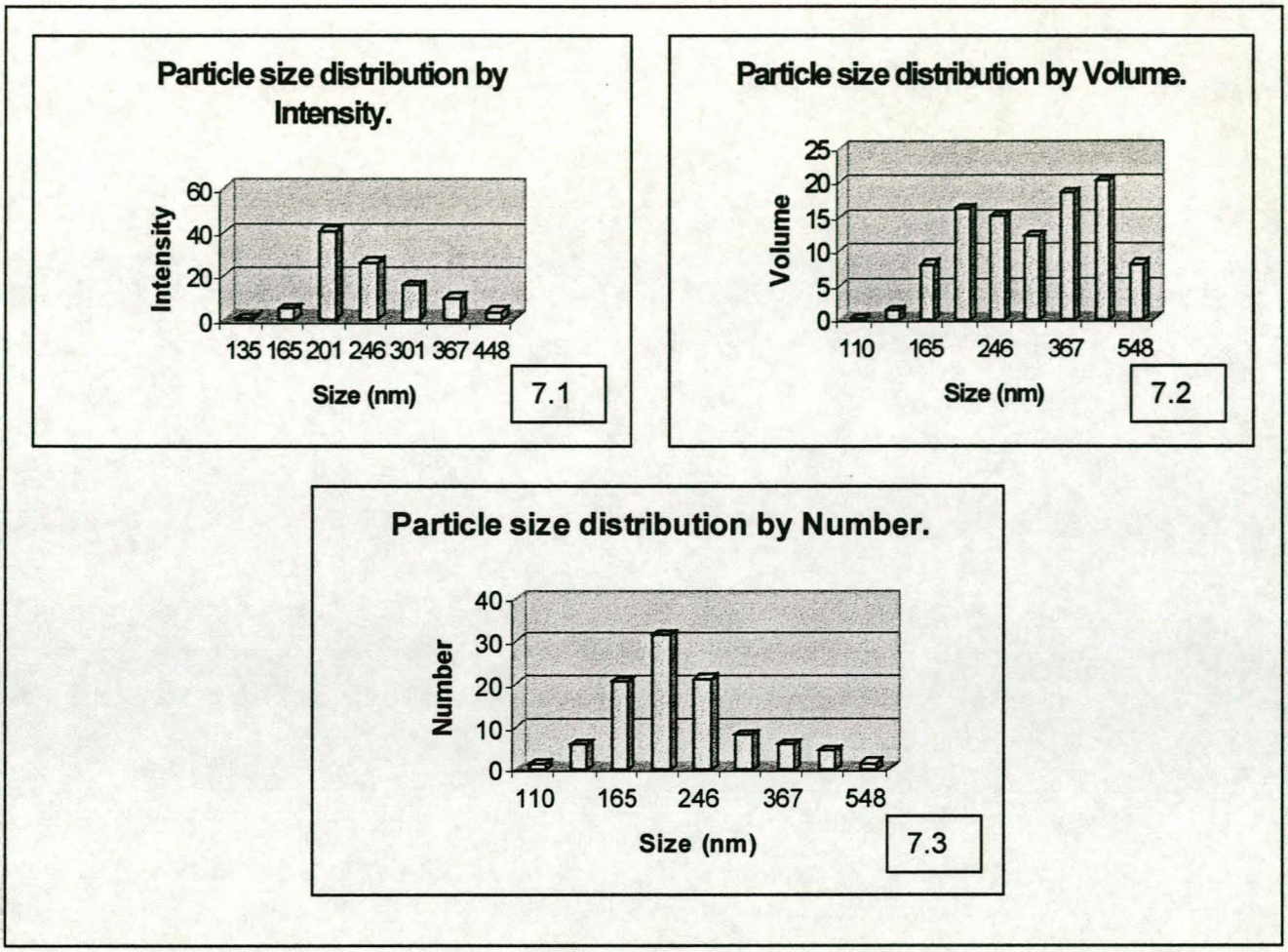
Table 7.1: Formulation used for the reaction of ENR50 with MMA, with the use of MAA as a graft site.

7.2.1.4 Analysis of the latex

A Malvern Zeta Sizer was used to determine the particle-size distribution.

7.2.1.5 Results and discussion

The zeta particle size average was 405.7 nm. By plotting the particle sizes against their intensities, volume and number a good approximation of their distribution was obtained as shown in Charts 7.1 to 7.3 (see Appendix 2).



Charts 7.1 to 7.3: Particle size distributions of particles formed during the reaction of MMA with ENR50.

Charts 7.1 to 7.3 show that the particle sizes vary from small (110 nm) to large (548 nm). Charts 7.1 and 7.2 also show clearly that the majority of particles have a diameter that varies between 160 and 450 nm.

7.2.2 HOMOPOLYMERIZATION OF METHYL METHACRYLATE

7.2.2.1 Aim

To investigate the particles-size of MMA during its homopolymerization.

7.2.2.2 Materials

MMA was hompolymerized to form polymethyl methacrylate by using commercially available monomer. Plascon supplied the MMA and MAA. Saarchem supplied NP100.

7.2.2.3 Synthetic procedure

The synthetic procedure used was the same as that used for the polymerization of MMA in the presence of ENR50 as reported earlier in this chapter, except for the exclusion of ENR50 in this experiment.

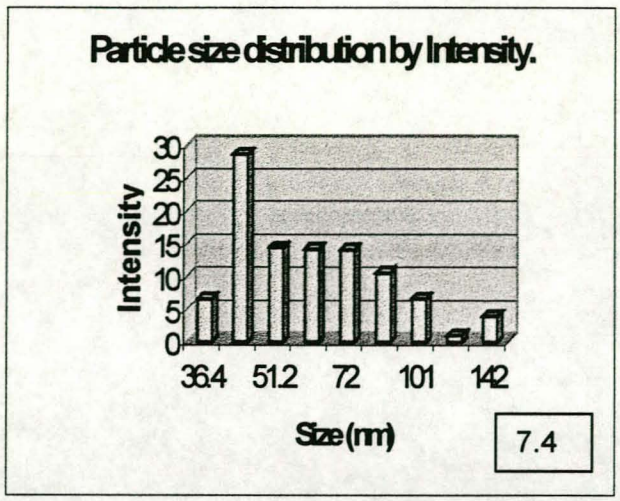
7.2.2.4 Analysis of the latex

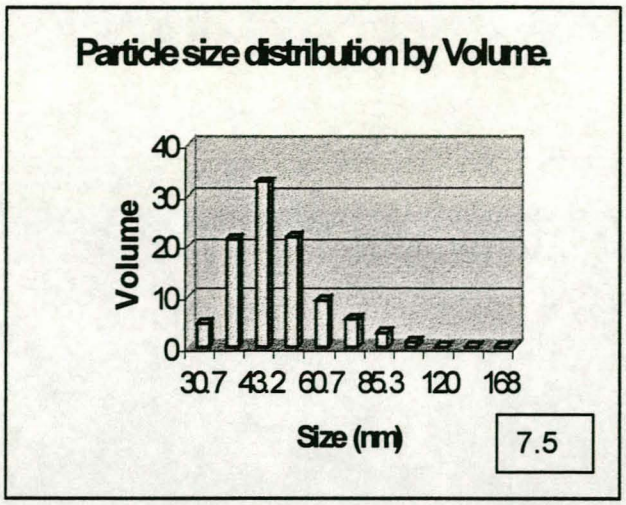
A Malvern Zeta Sizer was used to determine the particle-size distribution.

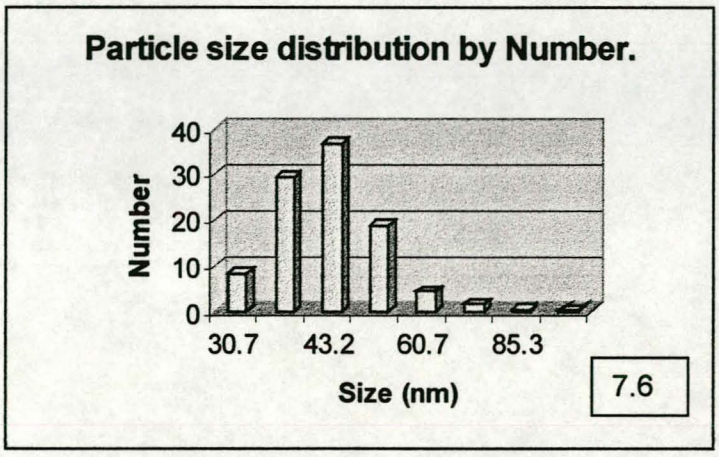
7.2.2.5 Results and discussion

The zeta particle size average shows a value of 55.7 nm. The particle sizes were again plotted against their intensity, volume and number to get an approximation of their distribution. See Charts 7.4 to 7.6 (see Appendix 2). The Charts show that the particle sizes vary between 30 and 140 nm with the majority between 30 and 60 nm.

As can be seen the results quoted in Section 7.2.1.5, the polymerization of MMA in the presence of ENR50 did not produce any particles close to the diameters obtained during the homopolymerization of MMA. We can therefore safely conclude that the reaction of







Charts 7.4 to 7.6: Particle size distributions of particles formed during the homopolymerization of MMA.

MMA with ENR50 does not produce any homopolymerized MMA. During the polymerization of MMA in the presence of ENR50, the MMA must therefore have reacted with the ENR50 particles. We can therefore conclude that MMA may have grafted onto the ENR50 particles.

7.2.3 SIMULTANEOUS DMA AND DEA ANALYSIS OF METHYL METHACRYLATE REACTED WITH ENR50

7.2.3.1 Aim

To investigate grafting in the reaction of MMA with ENR50 by simultaneous DMA and DEA analysis.

7.2.3.2 Materials

The methyl methacrylate and ENR50 were used as supplied. Plascon supplied the MMA and MAA. Saarchem supplied NP100. The ENR50 was filtered through cheesecloth to get rid of any grit that might be present.

The experimental details of the synthetic procedure and the preparation of cast films are as follows:

7.2.3.3 Synthetic procedure

This is the same as reported in Section 7.2.1.3 for the procedure used for the polymerization of MMA in the presence of ENR50. The formulation used is the same as in Table 7.1, except that the ratio of ENR : MMA : MAA was changed to 50 : 49 : 1.

7.2.3.4 Preparation for film casting

The latex was destabilized with methanol. The water was poured off and the rubber was dried overnight, at room temperature (23 °C) in a vacuum oven. The dried rubber was then redissolved in a mixture of ethylacetate and ethanol with a ratio of 2 : 1. An aluminium pan was then filled with this rubber and this was allowed to dry at room temperature (23 °C) to form a film. The reason behind the use of ethylacetate and ethanol in this specific ratio was that it is used, in industry, to dissolve the binders that are used with the propellants.

The cast film was cut into pieces suitable for analysis by a sharp razor blade with the edges lubricated with water.

A Perkin-Elmer 7e Dynamic Mechanical Analyzer and an Eumetric System III Microdielectrometer were used, simultaneously to obtain the dynamic mechanical and the dielectric measurements. The parameters used are summarised in Table 7.2.

Table 7.2: Parameters used in simultaneous DMA/DEA analyses.

Sample	Grafted ENR50	Disk
Instrumental	DMA	Perkin-Elmer DMA 7e with the DEA kit
	Measuring System	15 mm Cup and plate
	Geometry	Disk
Environmental	Purge	Nitrogen, (30 cc/min)
	Coolant	Liquid Nitrogen
Parameters	Mode	Temperature Scan
	Temperature Program	-60 to 160 °C at 5 C/min
	Static Force	Amplitude Control
	Dynamic Force	Amplitude Control
	Amplitude	8 µm
	Frequency	1.00 Hz

Instrumental	DEA	Micromet Eumetric System III DEA
	Interface	Mid Conductivity
Parameters	Sensor	Mono/User
	A/D ratio	7.1 cm
	Base Capacitance	20 pF
	Frequencies	1, 10, 50, 1000, 10000 Hz
	Cycle Time	15 seconds
	Duration	45 minutes

7.2.3.5 Results and discussion

Emulsion poymerization in the presence of a seed latex shows complex morphologies.

The tan δ and the modulus vs. temperature plots, from the DMA, for the polymerization reaction of ENR50 with MMA and MAA are shown in Figure 7.2. From these results we can see a complex three-phase system. The log permittivity vs. temperature plot, from the DEA, for this reaction is shown in Figure 7.3. Two phases are visible here.

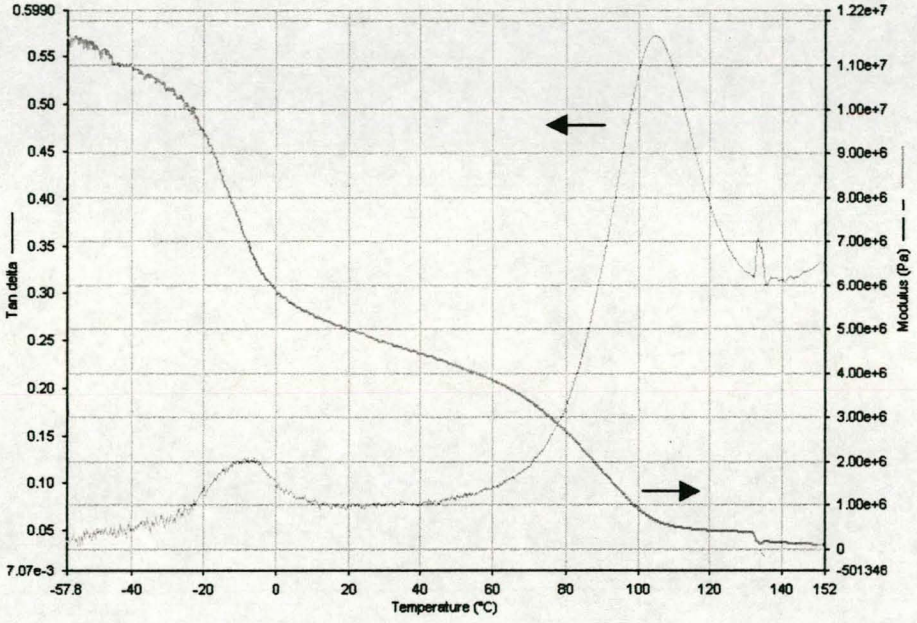


Figure 7.2: Tan δ and modulus vs. temperature plots for the reaction of ENR50 with MMA, with the use of MAA as a graft site.

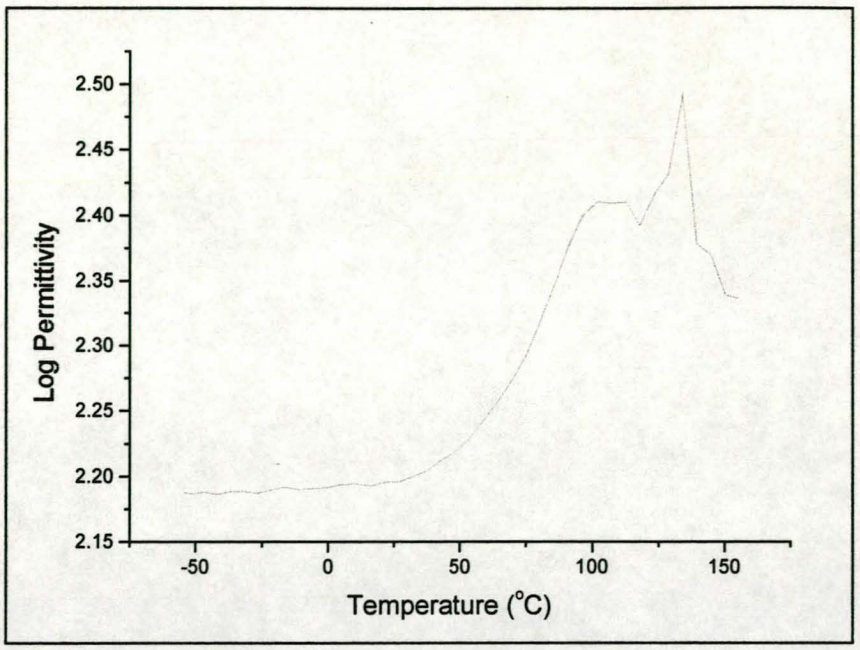


Figure 7.3: Log permittivity vs. temperature plot for ENR50/MMA/MAA.

The tan δ vs. temperature plot in Figure 7.2 clearly shows the rubbery phase (ENR50), the grafted PMMA phase and a peak at 134.4 °C. The latter is the result of MAA that has homopolymerized in the emulsion. This may be due to inadequate mixing of the pre-emulsion before the polymerization reaction was started. Phase separation is clearly in evidence due to the well-defined peaks. The tan δ vs. modulus plot in Figure 7.2 also shows sharp drops indicative of phase separation.

The log permittivity vs. temperature curve in Figure 7.3 only indicates two peaks, at 105 °C and at 134.4 °C, respectively. These are again the blend and nonblended grafted PMMA and the PMAA peaks, and the PMAA peak is large compared to that measured by the DMA. This is due to the analysis technique used. The DEA is very sensitive to dipoles and ions and therefore an acid such as PMAA will be prominent. The DEA however, does not show any rubbery peaks. Because the DEA is sensitive to dipoles we can conclude that the epoxy group concentration has been reduced, probably in a small portion of the rubber that did not mix with the grafted material. In the original

ENR50 the heterogeneous epoxidization of the latex particles appears to have left a less epoxidized core rubber particle that does not easily graft.

From these results it again appears as if the MAA has reacted with a few epoxide groups and that grafting has taken place from this site that was formed. The MAA reacts preferentially with the rubber that has the highest concentration of epoxidization i.e. the outer core of the latex particle. Grafting will only occur where MAA has formed the graft attachment site.

7.2.4 ANALYSIS OF MATERIAL FORMED DURING THE REACTION OF MMA WITH ENR50 BY THE GPEC TECHNIQUE

7.2.4.1 Aim

To investigate grafting in the reaction of MMA with ENR50 by the GPEC technique.

7.2.4.2 Materials and synthetic procedure

See Sections 7.2.1.2 and 7.2.1.3 for the materials and the synthetic procedure used respectively.

7.2.4.3 Analytical technique used

The most significant information regarding the grafted material can be obtained via non-exclusion chromatographic analyses, such as gradient polymer elution chromatography (GPEC) and liquid chromatography under critical conditions (LCCC). GPEC analyses on the grafted rubber were done at the Laboratory of Polymer Chemistry at the Eindhoven University of Technology. Analyses were carried out to determine the amount of grafting of PMMA onto the ENR. GPEC also served to fractionate the various components of the material (ungrafted rubber, PMMA grafted rubber, free PMMA) in order to further analyze these specific components.

GPEC works on the following principle:

The sample is absorbed onto a chromatographic column. A gradient of non-solvent and solvent are then pumped through the column. At the highest non-solvent and lowest solvent levels the fraction with the lowest molecular weight will emerge first. As the solvent levels are slowly increased the higher molecular weight fractions, as well as the grafted material, will emerge from the column.

The experimental set-up is shown in Figure 7.4.

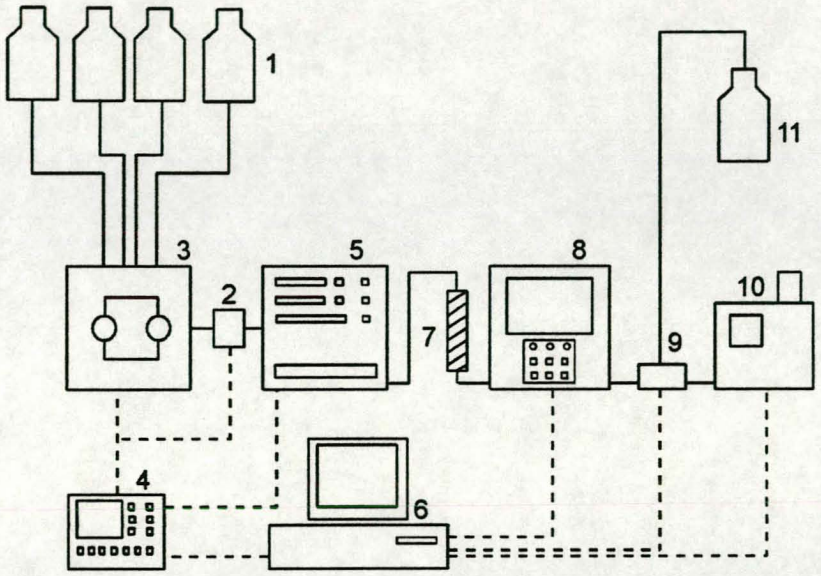


Figure 7.4: Schematic representation of a GPEC experimental set-up. Components are: (1) solvents, (2) mixing chamber, (3) gradient pump, (4) controller, (5) injector, (6) computer, (7) column, (8) UV detector, (9) switch valve, (10) ELSD detector, (11) solvent waste [8].

7.2.4.4 Results and discussion

The results of the GPEC analyses of the grafted rubber formed in the reaction of ENR50 with MMA are shown in Figure 7.5.

The surfactant, as indicated by the NP50 standard, emerges first from the column at a retention time of 10 minutes. At a retention time of about 18 minutes, as indicated by the PMMA standard, we find no peak for homopolymerized methyl methacrylate. At a retention time of 30 minutes, as indicated by the ENR50 standard, the ENR50 emerges from the column. The peaks emerging after 40 minutes are the result of gel fractions. The remaining peak at 27 minutes is therefore the peak of grafted ENR50. We know now from these and the DMA-DEA results (section 7.2.3.6) that we have unreacted rubber, grafted rubber and no homopolymer.

The above results are therefore a clear indication that grafting of ENR50 had taken place and that the pre-emulsion polymerization method used, produced very efficiently grafted material due to the formation of no homopolymerized methyl methacrylate.

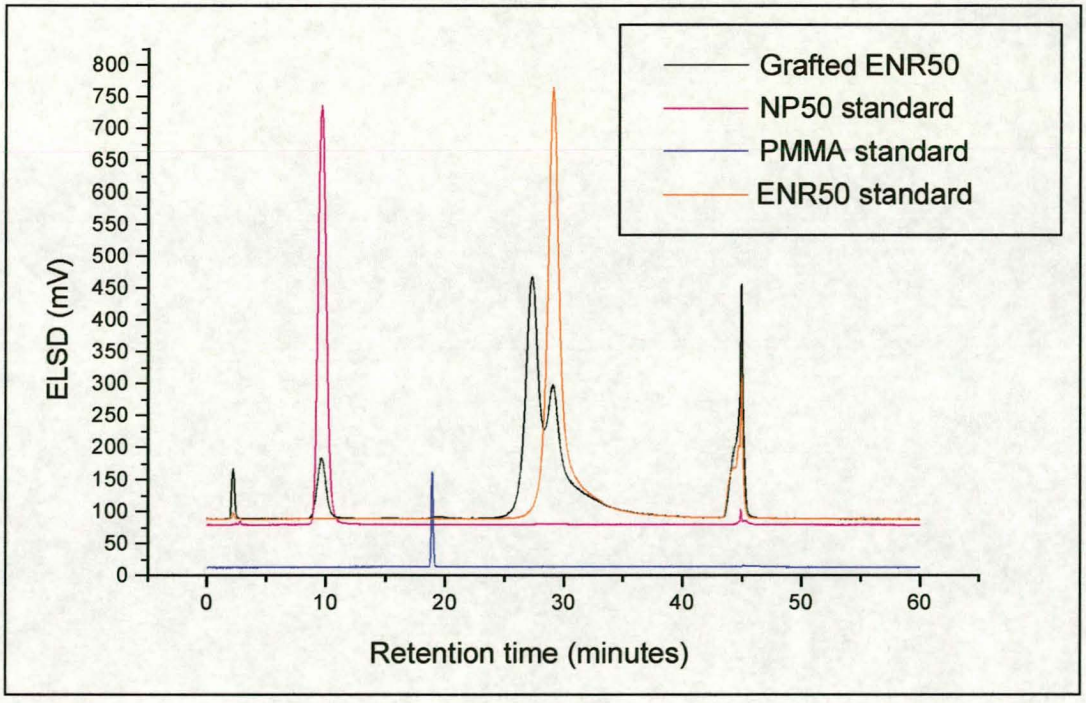


Figure 7.5: GPEC results of the grafted rubber formed in the reaction of MMA with ENR50.

7.3 CONCLUSIONS

1. Particle-size distribution analyses can be used as a possible indicator of grafting.
2. The use of the simultaneous DMA and DEA combination can be used as a quantitative indicator of grafting.
3. GPEC analyses conclusively show that grafting has taken place in the reaction of ENR50 with MMA, where MAA was used as a graft site initiator.
4. The pre-emulsion polymerization method used, produced very efficiently grafted rubber due to the formation of no homopolymerized methyl methacrylate, as demonstrated in Figure 7.5.

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CHAPTER 8

PHASE SEPARATION OF GRAFTED EPOXIDIZED NATURAL RUBBER

8.1 INTRODUCTION

The formation of grafted material during emulsion polymerization can lead to complex structures. This can be seen in core-shell material where one polymer forms a shell around the seed latex. As with other types of graft copolymers, some monomer dissolves within the seed latex. Upon polymerization, the second monomer phase-separates to yield a complex inner morphology, aptly named the "salami structure" for its crossectional resemblance to a slice of salami [1].

The grafted material that is formed during the reaction of methyl methacrylate with epoxidized natural rubber (ENR50) shows complex phase structures, probably a core-shell with the shell having a salami structure, as depicted in Figure 8.1. Since the morphology of heterophase polymers can be affected by the casting solvent and the nature of its interaction with the polymer [2], the physical properties of the cast rubber are also expected to depend on the casting solution. This is discussed in Chapter 9 where impact properties are investigated. A change in impact performance can be seen with a grafted material where a film was formed by casting from the latex and where film formation took place by using ethylacetate as casting solution.

Phase separation in a grafted latex depends on certain conditions e.g. molecular mass [3, 4], surfactants used and temperature. Different phase structures can be seen when surfactants with different HLB values are used and also where the latex cast films are heated, cooled and reheated again.

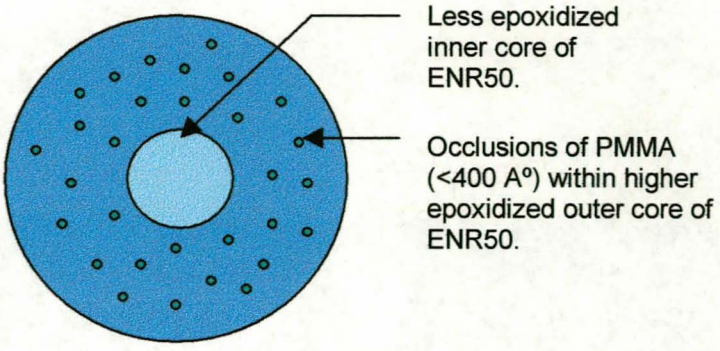

Figure 8.1: Possible cross-section of an ENR50 particle, grafted with PMMA, on a higher epoxidized outer core.

8.2 EXPERIMENTAL

8.2.1 DETERMINATION OF THE EFFECT OF THE USE OF DIFFERENT SURFACTANTS ON THE PHASE STRUCTURE OF GRAFTED ENR50 UPON LATEX CASTING

8.2.1.1 Aim

To investigate the effect of the use of NP30 and NP50 on the phase structure of grafted ENR50.

8.2.1.2 Materials and synthetic procedure

Tables 8.1 and 8.2 show the ingredients and formulations of the materials, and the pre-emulsion procedure is detailed in section 5.2.3 in Chapter 5.

8.2.1.3 Preparation for film casting

See Section 5.2.4 in Chapter 5.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	25.43	-	-
NP30 (Surfactant)	2.8	2.8	8
ENR50	47.73	26.25	75
MMA	8.4	8.4	24
MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 8.1: Pre-emulsion reaction of ENR50 with MMA where NP30 is used.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	25.43	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	47.73	26.25	75
MMA	8.4	8.4	24
MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 8.2: Pre-emulsion reaction of ENR50 with MMA where NP50 is used.

8.2.1.4 Results and discussion

The results of the reaction of ENR50 with MMA, where NP30 and NP50 were respectively used, can be seen in Figures 8.2 and 8.3. Where NP30 was used three tan delta peaks can be observed. NP30 is not a very high HLB-value surfactant, hence grafting may not have been that effective and the phases may therefore start to overlap. When NP50 is used in the reaction only two phases can be seen. NP50 has a higher HLB-value than NP30 and will therefore be more effective in graft formation. The phase-separated epoxidized rubber particles and the grafted PMMA therefore form the two phases seen.

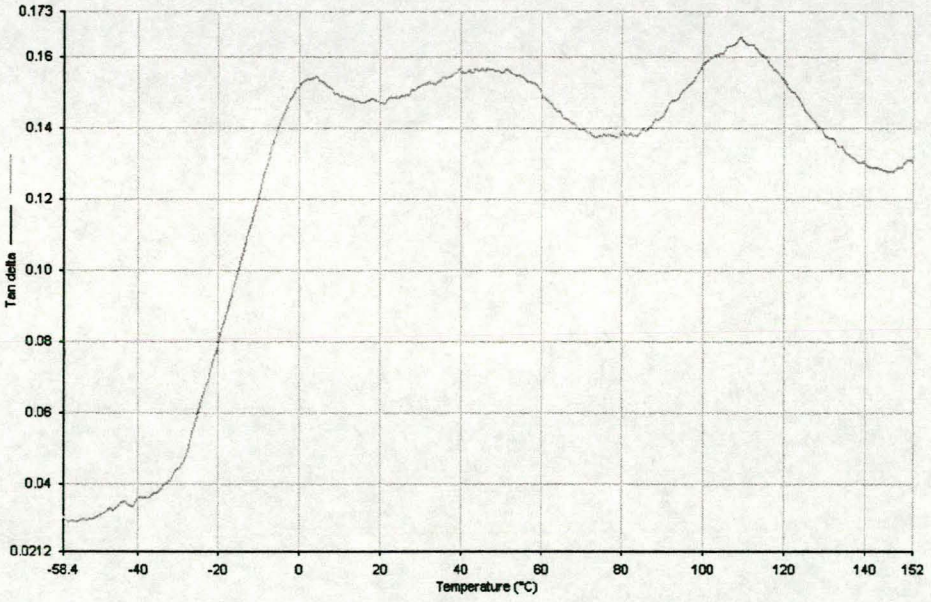

Figure 8.2: Effect of NP30 on phase structure of grafted rubber as determined by DMA 7e.

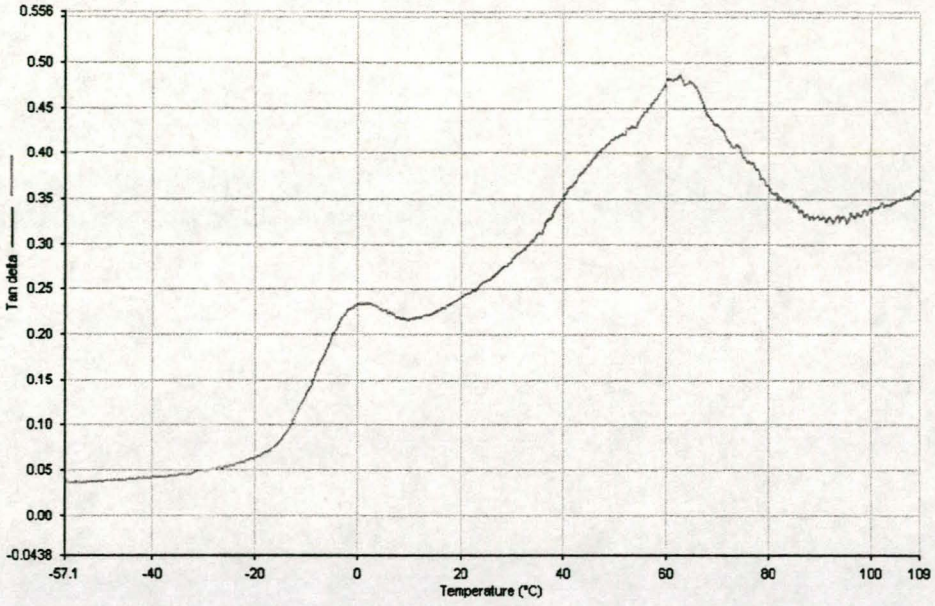

Figure 8.3: Effect of NP50 on phase structure of grafted rubber as determined by DMA 7e.

The cast latex films where NP30 and NP50 were respectively used, were used to perform a second run after the first run was performed with the DMA 7e. This was done to determine the effect of annealing on phase separation. The results are shown in Figures 8.4 and 8.5. When NP30 was used the annealing led to basically two phases. Where NP50 was used the annealing led to the formation of one peak. The poorer surfactant (NP30) therefore led to slightly more phase separation, whereas the better surfactant (NP50) led to a stronger blending of the separate phases.

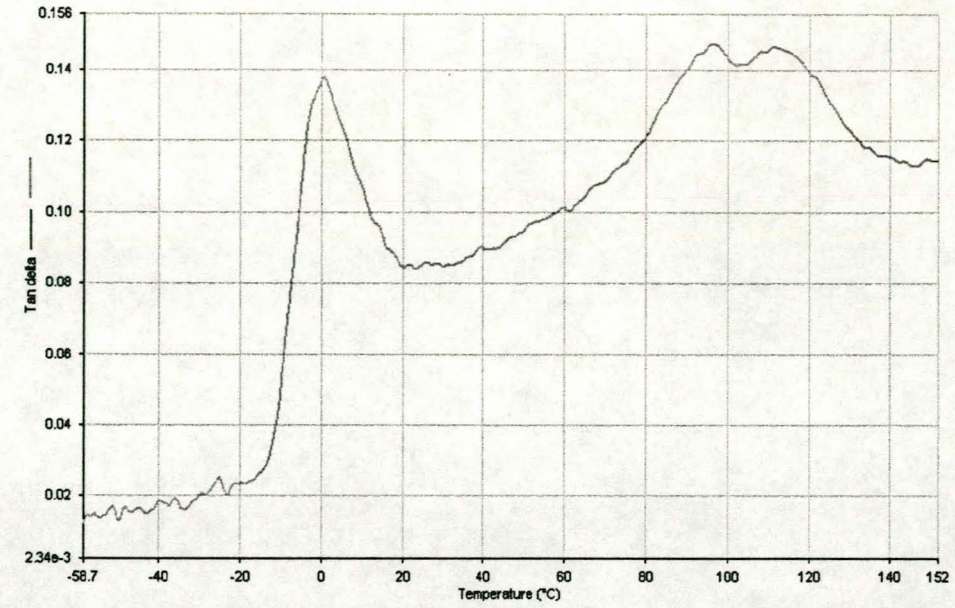

Figure 8.4: Effect of annealing on the cast latex film where NP30 was used.

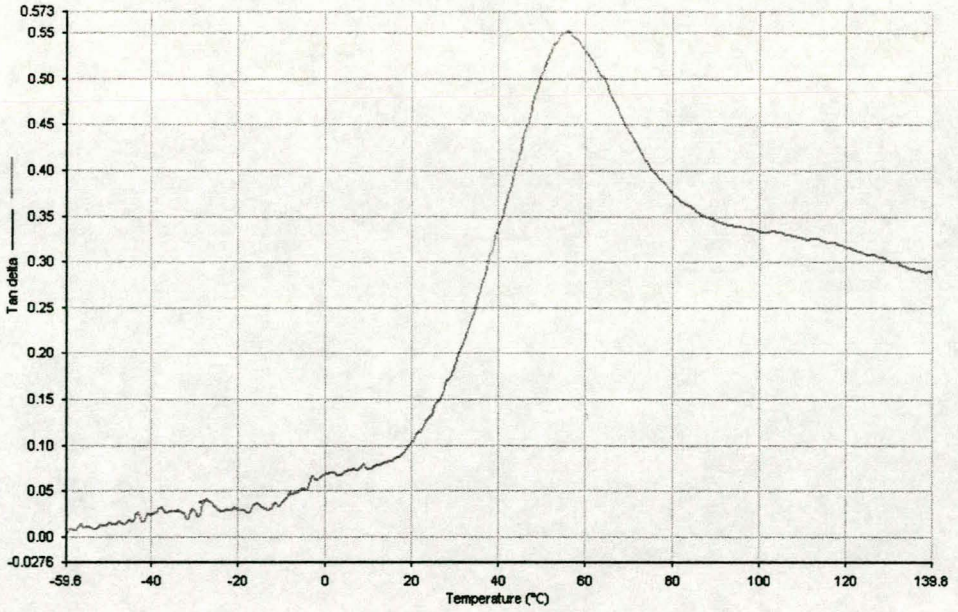

Figure 8.5: Effect of annealing on the cast latex film where NP50 was used.

8.2.2 DETERMINATION OF THE EFFECT OF THE USE OF DIFFERENT AMOUNTS OF MMA ON THE T_g OF THE GRAFTED ENR50

8.2.2.1 Aim

To investigate the effect of the use of gradually increased concentrations of MMA on the T_g of grafted ENR50.

8.2.2.2 Materials and synthetic procedure

See Tables 8.3 and 8.4, as well as the pre-emulsion procedure in Section 5.2.3 in Chapter 5.

8.2.2.3 Preparation for film casting

See Section 5.2.4 in Chapter 5.

A Perkin-Elmer 7e Dynamic Mechanical Analyzer was used for the dynamic mechanical measurements. The temperature range studied was from -60 to 160 °C. The heating rate was 5 °C/min and the frequency employed was 1 Hz.

8.2.2.4 Results and discussion

The results of using different amounts of MMA on the T_g of the grafted ENR50 can be seen in Figure 8.6. The amount of MMA used has a significant influence on the T_g of the grafted material.

As the amount of MMA is increased the T_g decreases as shown in Figure 8.7. This may be due to the non-random epoxidization of natural rubber [5]. The ENR may therefore consist of highly epoxidized natural rubber blocks and less epoxidized natural rubbery blocks. As the MMA content is increased, the separation of these blocks becomes more pronounced and the T_g tends to drop to the lower value of the less epoxidized natural rubber.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	25.43	-	-
NP100 (Surfactant)	2.8	2.8	8
ENR50	47.73	26.25	75
MMA	8.4	8.4	**24**
MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 8.3: Pre-emulsion reaction of ENR50 with MMA where 24% MMA is used.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP100 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	**49**
MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 8.4: Pre-emulsion reaction of ENR50 with MMA where 49% MMA is used.

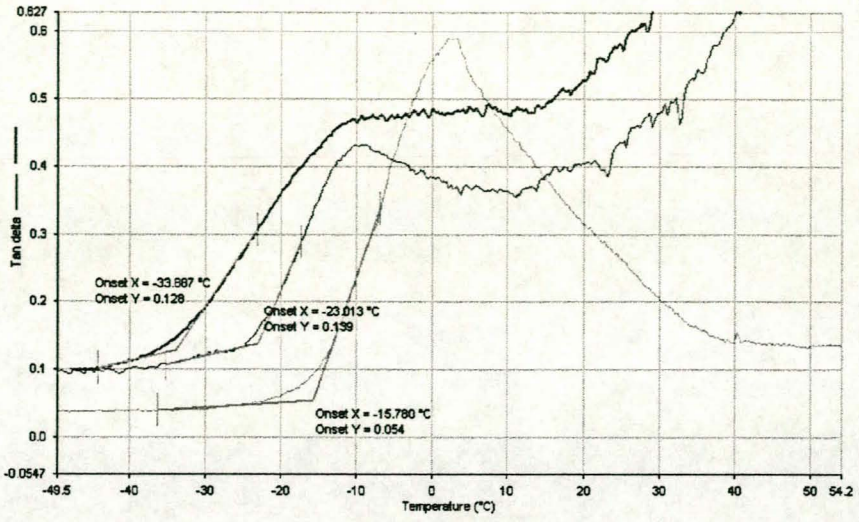

Figure 8.6: The effect of the amount of MMA in pre-emulsion polymerization on the T_g of the cast latex film as determined by DMA 7e.

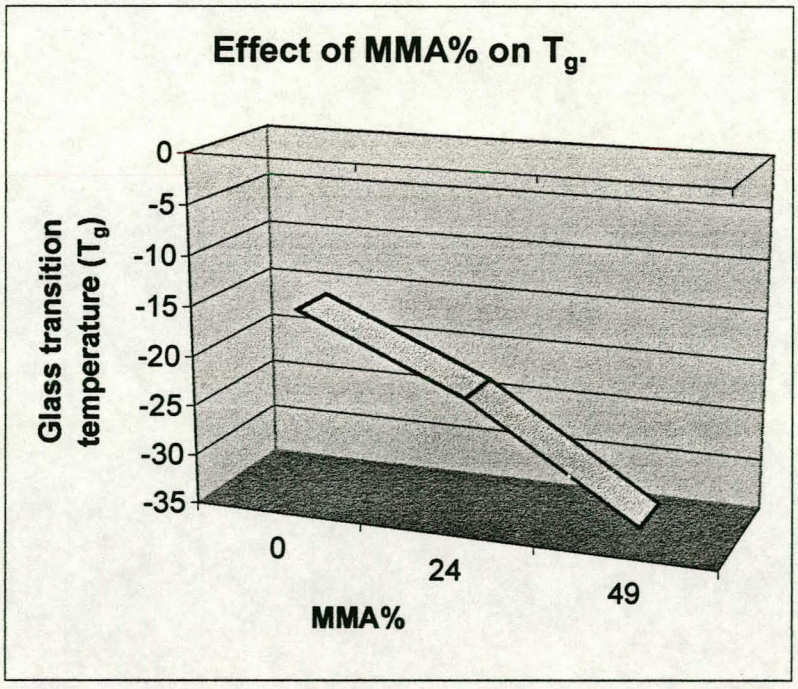

Figure 8.7: Effect of MMA% in pre-emulsion polymerization on the T_g of the cast latex film.

8.3 CONCLUSIONS

1. High HLB-value surfactants (NP50) are more effective in graft formation, in the reaction of ENR50 with MMA, than low HLB-value surfactants.
2. Upon annealing high HLB-value surfactants (NP50) led to a blending of phases, whereas low HLB-value surfactants (NP30) led to more phase separation.
3. An increase in MMA concentration led to a decrease in the T_g of the cast latex film.

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CHAPTER 9

IMPACT RESISTANCE OF THE GRAFTED EPOXIDIZED NATURAL RUBBER

9.1 INTRODUCTION

The major interest in the two phase systems of grafted epoxidized natural rubber (ENR) with methyl methacrylate (MMA) centres on the ability of dispersed particles of a rubbery phase to improve the impact strength of a glassy matrix without corresponding plasticization. In an early attempt to explain the impact properties of polyblends Merz *et al.* [1] incorrectly attributed the impact strength of the composites to the ability of the rubber to hold the crack faces together. It is easily seen from stress-strain curves that the rubber, at strains up to failure point, can absorb only minor amounts of energy. The whitening which often accompanies the deformation or fracture of rubber modified plastics suggested an alternate energy absorption mechanism to Schmitt and Keskkula [2], who proposed that the whitening and energy absorption arose from the formation of many microcracks in the immediate vicinity of the rubber particles.

Newman and Strella [3] ascribed the increased energy absorption in rubber-modified plastics to the increased cold-drawing of the glassy matrix polymer. They associated this increased cold drawing with an increase in free volume of the matrix near the rubber particle when subjected to stress. This increase in free volume was postulated to occur because a rubber particle with a Poissons' ratio close to 0.5 resists volume change. If the bulk volume expansion of the strained sample is to be maintained at its observed level the lack of volume change in the rubber must be compensated for by an accentuated expansion of the matrix immediately surrounding the rubber particles. This surrounding material is then effectively nearer its glass transition temperature, it can be deformed more easily, and absorbs more energy in viscous flow processes.

The discovery of crazing as a fracture process in glassy plastics lead to the proposal by Bucknall and Smith [4] that rubber particles' increased toughness is brought about by inducing greater crazing prior to fracture. Since the local orientation processes

associated with crazing involves considerable viscous-energy dissipation, the increased degree of crazing is accompanied by greater energy absorption.

Brogan [5] differed from the multiple craze theory; he proposed a mechanism whereby rubber dispersions greatly increased the energy absorbing volume of two phase systems by causing cracks or crazes to branch dynamically at rubber sites through the Joffe mechanism [6].

The multiple crazing theory is, however, well founded on experimental evidence and successfully explains the impact and tensile properties of high impact polystyrene (HIPS), including stress whitening, decreases in density and elongation without lateral contraction [7]. The effects of rubber content, particle size and size distribution, temperature and rubber to matrix adhesion can all be understood in terms of the theory [7].

It has been shown that crazing is not always the dominant mechanism for deformation. Shear yielding plays an increasingly important role in the impact resistance of the more ductile polymers such as ABS (acrylonitrile-butadiene-styrene) terpolymers and PVC [8]. Rubber-modified PVC does not necessarily exhibit crazing on impact [8]. Shear yielding is important for two reasons. Firstly, shearing provides an effective means of energy dissipation via orientation of polymer chains without the weakening effect of void formation as associated with crazes. Secondly, the orientation within a shear band is roughly parallel to the applied stress and thus normal to the plane of the crazes. Shear bands serve as obstacles to craze propagation. Shear bands can initiate at the highly stressed tip of a craze, thus bringing craze propagation to a halt [9]. Thus shear bands are seen to perform the functions associated with the rubber particles namely: initiation of crazes and prevention of catastrophic craze or crack growth.

Based on evidence presented it seems probable that impact strength in rubber-modified plastics depends on the relative contribution of crazing and shear yielding in a modified system, with shearing being the most efficient energy-absorbing mechanism [10]. This is illustrated when comparing the properties of the three most common types of impact resistant thermoplastics. According to Manson and Sperling [10] the impact strength of many HIPS materials are usually between 8-10 kJm^{-2}, ABS values are usually between

21-43 kJm^{-2} and high impact PVC has values over 53 kJm^{-2}. These values may be related to the principle means of toughening: HIPS mainly crazes on stressing, ABS exhibits a combination of crazing and shearing and rubber-toughened PVC exhibits primarily shearing [10].

A novel method has been used to characterize the impact performance of the grafted ENR50 that is independent of the total rubber content. This method was initially developed by Bair and Twombly [11], who employed it to evaluate the impact performance of four ABS terpolymers. The results obtained correlated well with those of standard Izod impact tests [11].

9.2 EXPERIMENTAL

9.2.1 EFFECT OF AA AND MAA ON THE IMPACT-RESISTANCE OF UNGRAFTED AND GRAFTED ENR50

9.2.1.1 Aim

To investigate the effect of AA and MAA on the impact performance of ungrafted and grafted ENR50.

9.2.1.2 Materials and synthetic procedure

See Tables 9.1 and 9.2, as well as the pre-emulsion procedure in Section 5.2.3 in Chapter 5.

9.2.1.3 Preparation for film casting

See Section 5.2.4 in Chapter 5.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	49
AA	0.35	0.35	**1**
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 9.1: Pre-emulsion reaction of ENR50 with MMA with AA as graft site initiator.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	49
MAA	0.35	0.35	**1**
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	======	=====	
	106.41	38.5	

Table 9.2: Pre-emulsion reaction of ENR50 with MMA with MAA as graft site initiator.

9.2.1.4 Results and discussion

In Chapter 5, AA and MAA were compared with regard to their influence on the reaction of MMA with ENR50. From the results in Chapter 5 (Section 5.3) it was decided to continue reactions with MAA. Figures 9.1 to 9.4 show the loss modulus vs. temperature curves where AA and MAA were used in the polymerization reaction of MMA with ENR50. See Table 9.3 for a summary of the impact-resistance results.

Table 9.3: Evaluation of the areas of the loss modulus peaks (Figures 9.1 to 9.4).

	Ungrafted ENR50		Grafted ENR50	
	AA	MAA	AA	MAA
Level of MMA used was 49%				
Area of loss modulus peak (Pa x min)	1.04×10^5	6.68×10^5	7.72×10^6	5.84×10^6
Temp. of loss modulus peak (°C)	-10.3	-7.5	74.1	77.5

The ungrafted and grafted rubber phases correspond well according to the temperature of the loss modulus peaks. There is a bigger difference between the area of the loss modulus peak of the ungrafted rubber phase than for the grafted rubber phase. As in the case of AA, the ungrafted rubber phase would be the restricting factor, it was decided to use MAA for further studies because of the bigger loss modulus area and therefore the higher impact resistance.

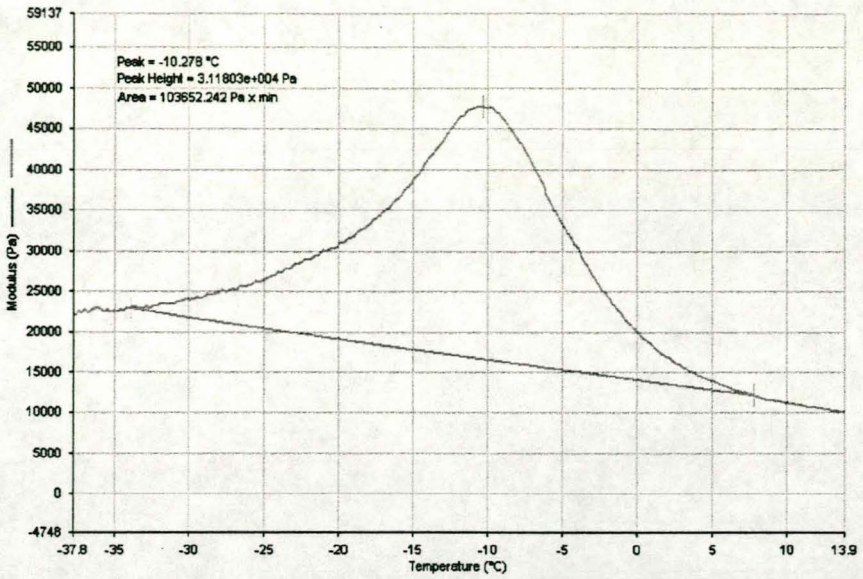

Figure 9.1: Loss modulus vs. temperature curve for ungrafted ENR50 where AA was used.

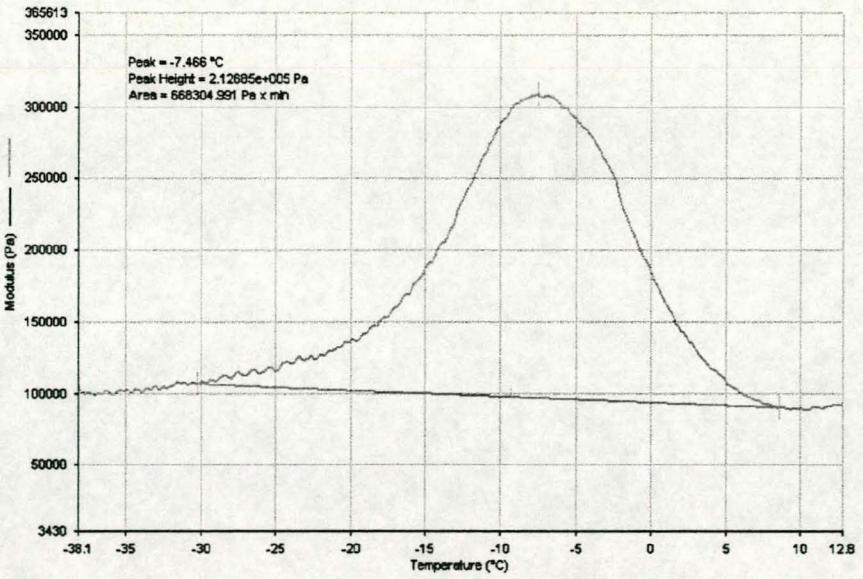

Figure 9.2: Loss modulus vs. temperature curve for ungrafted ENR50 where MAA was used.

Figure 9.3: Loss modulus vs. temperature curve for grafted ENR50 where AA was used.

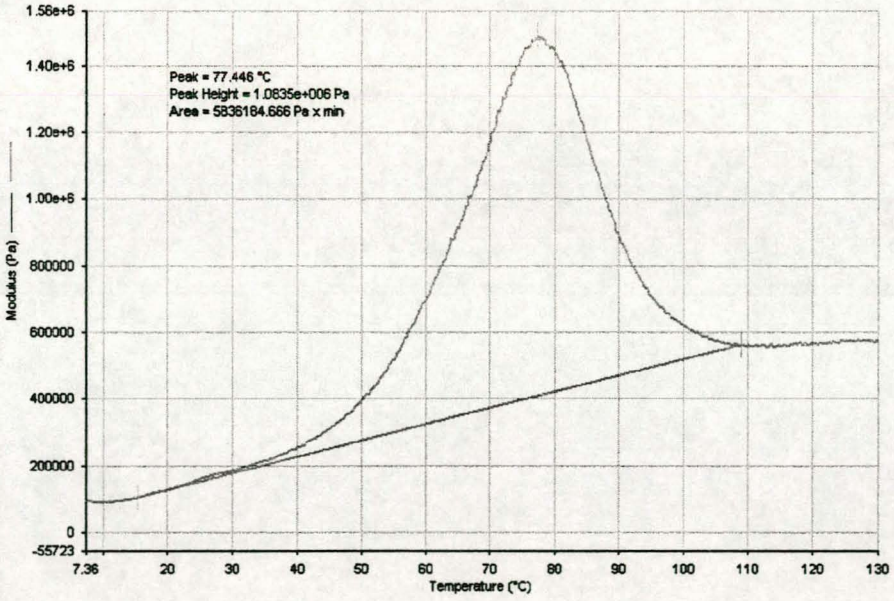

Figure 9.4: Loss modulus vs. temperature curve for grafted ENR50 where MAA was used.

9.2.2 EFFECT OF DIFFERENT TYPES OF SURFACTANT ON THE IMPACT RESISTANCE OF UNGRAFTED AND GRAFTED ENR50

9.2.2.1 Aim

To investigate the effect of different surfactants (NP30 and NP50) on the impact resistance of ungrafted and grafted ENR50.

9.2.2.2 Materials and synthetic procedure

See Tables 8.1 and 8.2, as well as the pre-emulsion procedure in Section 5.2.3 in Chapter 5.

9.2.2.3 Preparation for film casting

See Section 5.2.4 in Chapter 5.

A Perkin-Elmer 7e Dynamic Mechanical Analyzer was employed for the dynamic mechanical measurements. The temperature range studied was from -60 to 160 °C for both systems. The heating rate was 5 °C/min and the frequency employed was 1 Hz.

9.2.2.4 Results and discussion

Figures 9.5 to 9.8 show the loss modulus vs. temperature curves where NP30 and NP50 were used in the polymerization reaction of MMA with ENR50. Results are summarized in Table 9.4.

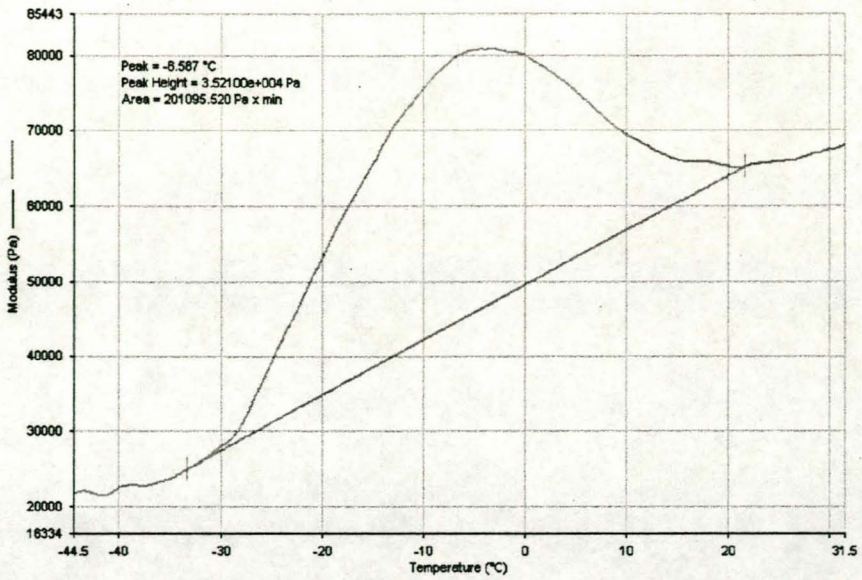

Figure 9.5: Loss modulus vs. temperature curve for ungrafted ENR50 where NP30 used.

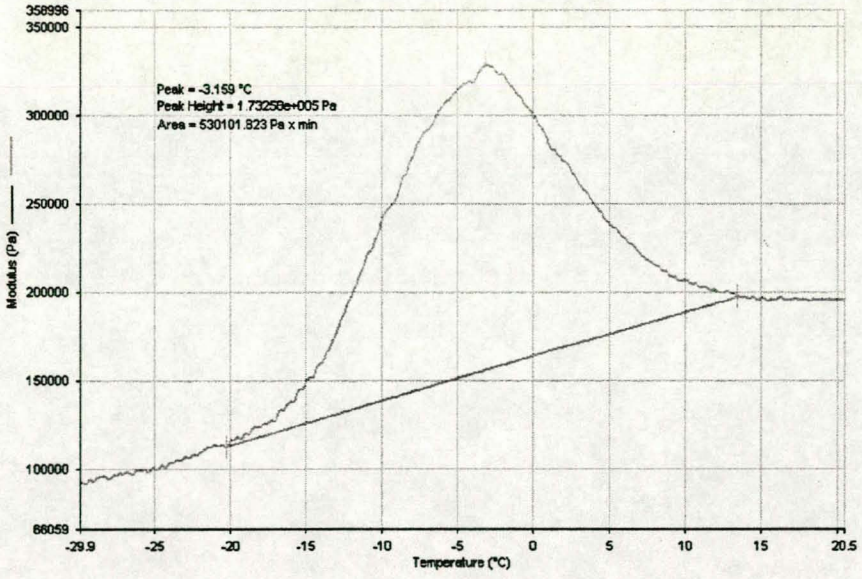

Figure 9.6: Loss modulus vs. temperature curve for ungrafted ENR50 where NP50 was used.

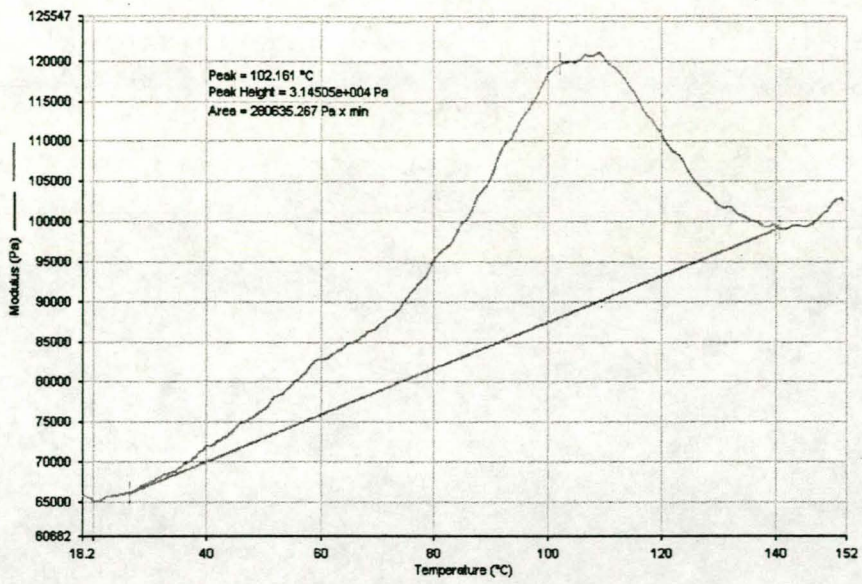

Figure 9.7: Loss modulus vs. temperature curve for grafted ENR50 where NP30 was used.

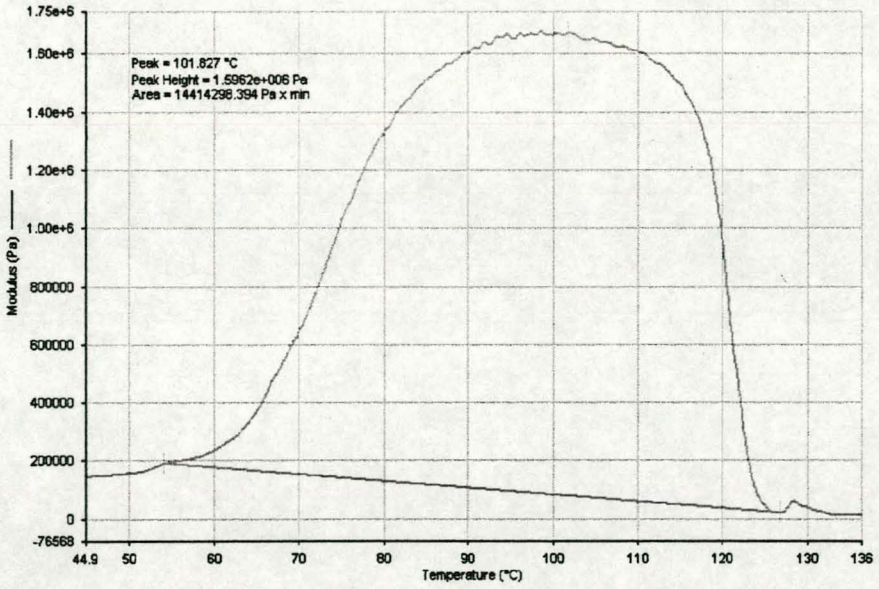

Figure 9.8: Loss modulus vs. temperature curve for grafted ENR50 where NP50 was used.

Table 9.4: Evaluation of the areas of the loss modulus peaks (Figures 9.5 to 9.8).

	Ungrafted ENR50		Grafted ENR50	
	NP30	NP50	NP30	NP50
Level of MMA used was 24%				
Area of loss modulus peak (Pa x min)	2.01×10^5	5.30×10^5	7.72×10^6	1.44×10^7
Temp. of loss modulus peak (°C)	-6.6	-3.2	102.2	101.8

From Table 9.4 it is seen that the ungrafted and grafted rubber phases correspond well according to the temperature of the loss modulus peaks. The areas of the loss modulus peaks of the ungrafted and the grafted rubber phases, where NP50 is the surfactant, are in both cases higher than for NP30.

The higher values (hence higher impact performance) can be explained in terms of their HLB values. See Chapter 2, Sections 2.7.2.1 and 2.7.2.3. NP50 has a higher HLB value than NP30. This means that NP50 has a higher solubility performance than NP30. The ENR50 latex is therefore more stable and more efficient grafting can take place between the rubber and the methyl methacrylate. This higher grafting efficiency leads to a higher impact resistant material. This can be seen clearly from the higher loss modulus peak areas. It can be seen from this that the type of nonyl phenol (surfactant) used is critical in impact performance. The higher the HLB value, the better.

By comparing the results in Tables 9.3 and 9.4 it is shown that the reaction between ENR50 and MMA, (where the MMA levels are moderate and where the surfactant has the highest HLB value) will lead to the best impact performance material.

9.2.3 EFFECT OF ETHYLACETATE AS CASTING SOLUTION SOLVENT ON THE IMPACT RESISTANCE OF UNGRAFTED AND GRAFTED ENR50

As ethylacetate and ethanol, in the ratio of 2 : 1, are used in the industry to dissolve the binders that are used with propellants, the effect of this mixture on the impact performance of ungrafted and grafted ENR50 was tested.

9.2.3.1 Aim

To investigate the effect of ethylacetate, with the use of different surfactants (NP50 and NP100) and different amounts of MMA (24% and 49%), on the impact resistance of grafted ENR50.

9.2.3.2 Materials and synthetic procedure

See Tables 8.2, 8.4 and 9.2, as well as the pre-emulsion procedure in Section 5.2.3 in Chapter 5.

9.2.3.3 Preparation for film casting

See Section 7.2.3.4 in Chapter 7.

A Perkin-Elmer 7e Dynamic Mechanical Analyzer was used for the dynamic mechanical measurements. The temperature range studied was from -60 to 160 °C. The heating rate was 5 °C/min and the frequency employed was 1 Hz.

9.2.3.4 Results and discussion

Figures 9.9 to 9.14 show the loss modulus vs. temperature curves for ungrafted and grafted ENR50 where ethylacetate was used as solvent for the preparation of the casting solution. See Table 9.5 for a summary of the results.

Table 9.5: Evaluation of the areas of the loss modulus peaks (Figures 9.9 to 9.14).

	Ungrafted ENR50		Grafted ENR50	
	NP50	NP100	NP50	NP100
Level of MMA used was 49%				
Area of loss modulus peak (Pa x min)	8.77×10^5	3.01×10^6	8.55×10^5	2.04×10^6
Temp. of loss modulus peak (°C)	-11.4	-15.0	107.1	92.5
Level of MMA used was 24%				
Area of loss modulus peak (Pa x min)	8.68×10^6	N/A	7.91×10^6	N/A
Temp. of loss modulus peak (°C)	-7.9	N/A	98.3	N/A

From Table 9.5 it can be seen that where a ***49% MMA*** level was used, the temperature of the ungrafted loss modulus peaks correspond well to each other, namely 11.4 °C and -15.0 °C, where NP50 and NP100 are used respectively. The grafted rubber peak where NP100 was used shows a lower temperature (92.5 °C), and this may be an indication that this grafted polymer will be useful at a slightly lower temperature than NP50-grafted ENR. The loss modulus peak areas of NP100 are, however, in both cases higher than those for the NP50. This is a clear indication that NP100 will lead to a higher

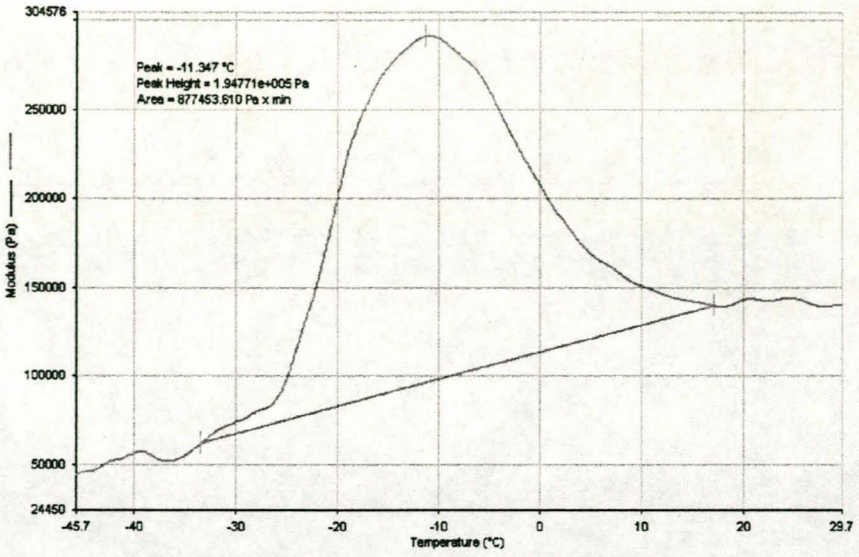

Figure 9.9: Loss modulus vs. temperature curve for ungrafted ENR50 where NP50 and 49% MMA was used.

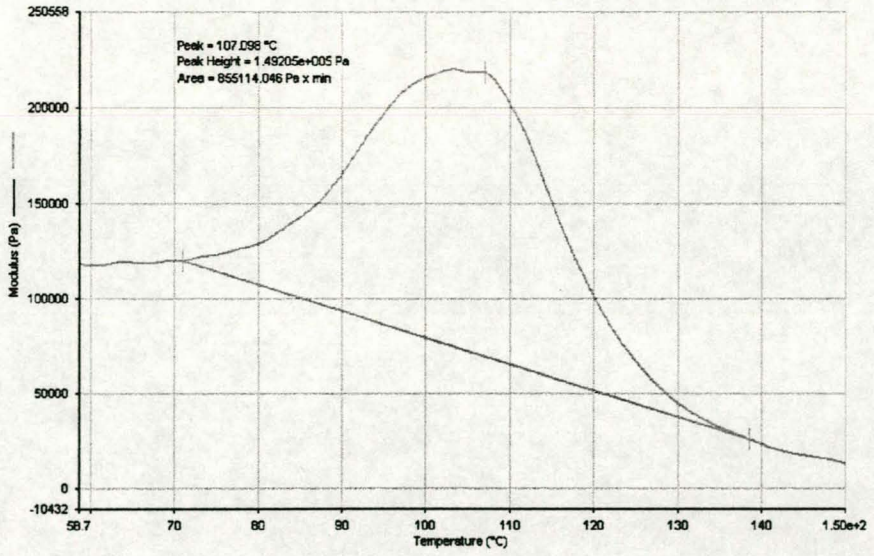

Figure 9.10: Loss modulus vs. temperature curve for grafted ENR50 where NP50 and 49% MMA was used.

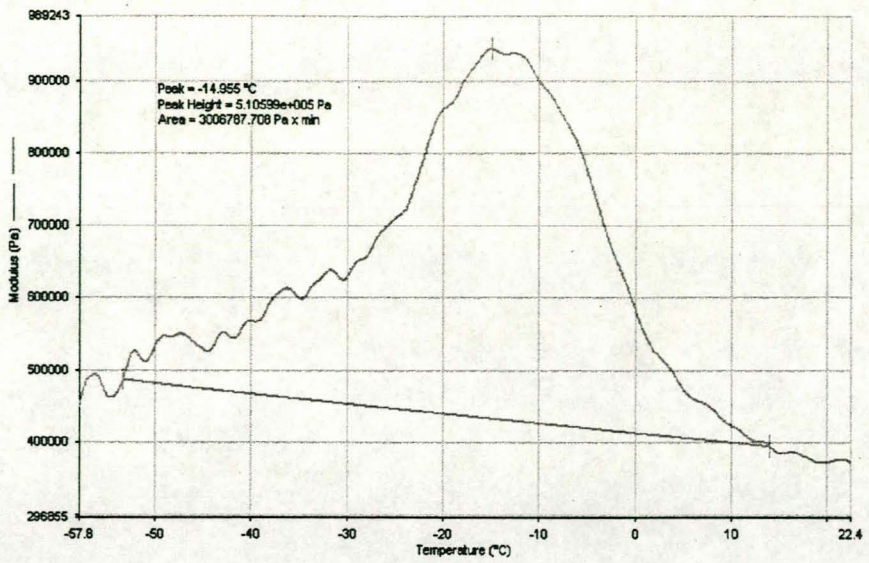

Figure 9.11: Loss modulus vs. temperature curve for ungrafted ENR50 where NP100 and 49% MMA was used.

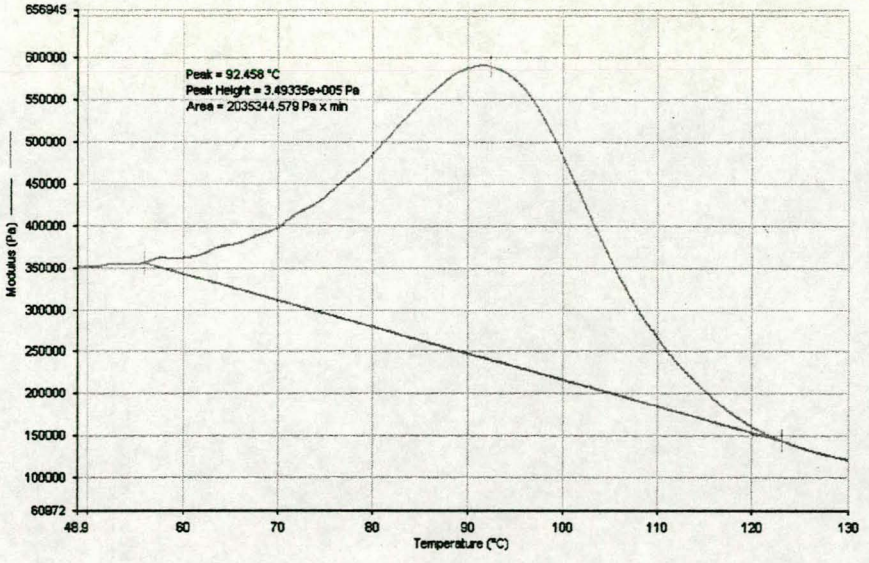

Figure 9.12: Loss modulus vs. temperature curve for grafted ENR50 where NP100 and 49% MMA was used.

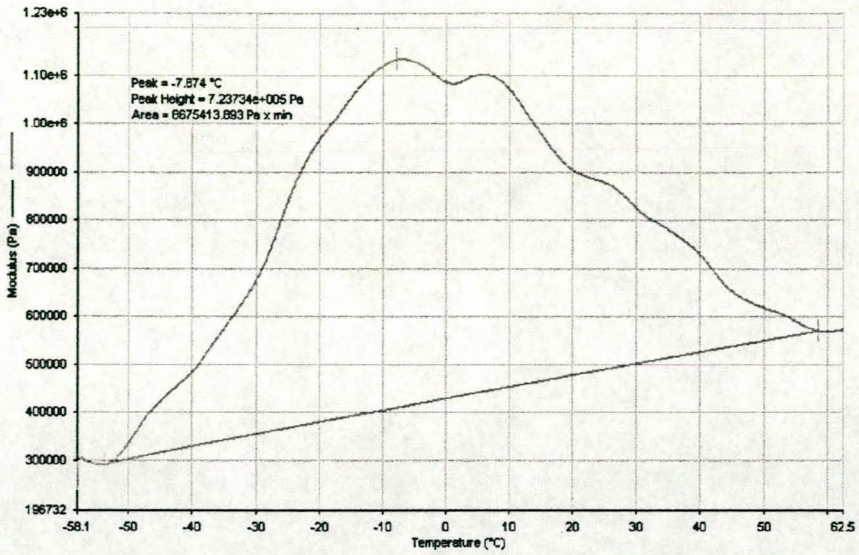

Figure 9.13: Loss modulus vs. temperature curve for ungrafted ENR50 where NP50 and 24% MMA was used.

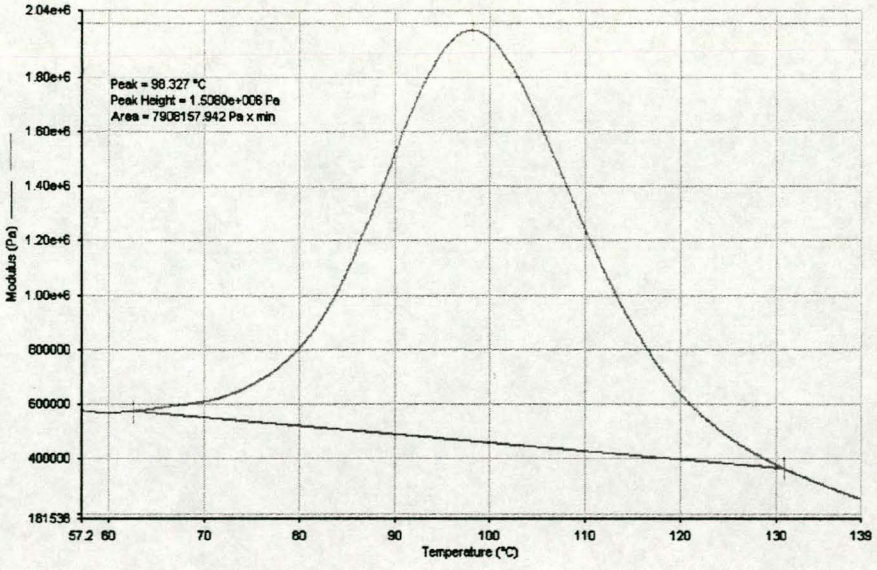

Figure 9.14: Loss modulus vs. temperature curve for grafted ENR50 where NP50 and 24% MMA was used.

impact-performance material than NP50, and again this can be explained in terms of HLB values (see paragraph 9.2.2.4). Seeing that the temperature of the NP100-grafted rubber phase is only slightly lower than for that of the NP50, it would be prudent to rather use NP100 for impact performance above NP50.

From Table 9.5 it can be seen that where a ***24% MMA*** level was used, the onset and peak temperatures of the loss modulus of the ungrafted rubber phase are higher, and for the grafted rubber phase lower than where 49% MMA was used. These temperature levels are, however, not that critical. The areas of the loss modulus peaks are however much higher than those where 49% MMA was used (this is true for NP50 and NP100) and therefore levels of 24% will lead to better impact performance.

9.3 CONCLUSIONS

1. High HLB-value surfactants (NP100) led to better impact performance grafted rubber than low HLB-value surfactants.
2. Ethylacetate, used as casting solution solvent, led to better impact performance material than latex casting.
3. MMA levels can be kept relatively low (24%) to produce grafted rubber with adequate impact performance.

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11. H. E. Bair and B. Twombly, Correspondence with B. Twombly, Perkin-Elmer, USA.

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

- A prerequisite of the study was to carry out a full literature review on ENR, and to determine whether it was possible to use an emulsion polymerization technique for the grafting reaction of MMA with ENR latex, to yield a material that is useful as a LOVA binder at low and high temperatures for the absorbance of impact.
  - The literature study revealed that the above hasn't been attempted before in an emulsion reaction.
  - Batch polymerization of ENR50 with MMA is not successful due to the destabilization of latex at too high levels of MMA and inadequate control of the reaction.
  - The delayed addition of monomer and the pre-emulsion technique can be successfully used as an emulsion polymerization technique for the grafting reaction of MMA with ENR latex.

- GPEC analyses of the material formed during the reaction of ENR50 with MMA, showed conclusively that grafting had taken place. The grafting of ENR in latex form can therefore be done by a vinyl monomer. GPEC analyses also revealed that the pre-emulsion polymerization method used, produced very efficiently grafted rubber due to the formation of no homopolymerized MMA.
  - Particle-size distribution analyses can be used as a possible indicator of grafting in emulsion polymerization.
  - The use of the simultaneous DMA and DEA combination can be used as an indicator of grafting in emulsion polymerization.

- A thermoplastic elastomer with dampening properties at low (about -25 °C) and high (about 80 °C) temperatures can be produced through the use of MMA and ENR50.
  - The technique involving the delayed addition of monomer led to a grafted material with a lower T_g than that of the product of the pre-emulsion technique.
  - The pre-emulsion technique can be used to produce a grafted material with higher dampening properties than those produced through the delayed addition of monomer technique.
  - By increasing the MMA levels the T_g of the grafted material can be shifted to a lower temperature.

- Through the use of the tan delta and loss moduli vs. temperature curves (in Chapter 5) and the GPEC results (in Chapter 7) we can conclude the following on the process of grafting of MMA onto ENR:
  - PMMA grafts onto the higher epoxidized outer core of ENR50.
  - A part of this grafted PMMA phase-separates as indicated by the loss moduli curves (in Chapter 5).

- The use of separate and simultaneous DMA-DEA analyses led to valuable insight into the make-up of the ENR used and the grafted material. These analyses (Chapters 5 to 8) show that ENR must be non-randomly epoxidized. As an analytical tool the DMA-DEA can subsequently be used to choose the best polymerization technique available and to fine-tune the formulation used for specific end-use conditions, e.g. type of acid used for graft site formation, type of surfactant and amount of monomer used.

- Ungrafted rubber and phase-separated grafted-PMMA are present in the grafted material formed during the reaction of MMA with ENR, as indicated by the loss moduli curves (in Chapter 5).

- The impact performance of the grafted material can be determined by calculating the area of the loss moduli curves. These results show that:
  - High HLB-value surfactants (NP100) led to better impact-performance grafted rubber than low HLB-value surfactants.

- Ethylacetate, used as casting solution solvent, led to a better impact performance material than latex casting.
- MMA levels can be kept relatively low (24%) to produce grafted rubber with adequate impact performance.

10.2 RECOMMENDATIONS

Due to ENR25's low T_g it is recommended that it be used in further grafting reactions with MMA. This will lead to grafted material with an impact resistance at a lower temperature. The use of other graft-site initiators i.e. peracids, where temperature can be used to start the reaction, are recommended.

It is also recommended that a full study of the effect of the materials used in the emulsion polymerization be done, to obtain a better understanding of the effects of these materials on graft formation and subsequent mechanical properties of the grafted ENR50.

The effect of MMA chain lengths on the phase separation of ENR50 needs to be looked at.

The DMA and DEA analyses can also be used to form time/temperature superpositioning curves for the mechanical and electrical behaviour of the grafted ENR50 to predict the long-term effects on the grafted ENR properties.

APPENDIX 1

DMTA CURVES FOR THE DETERMINATION OF THE COMPATIBILITY OF EPOXIDIZED NATURAL RUBBER WITH POLYMETHYL METHACRYLATE AND POLYSTYRENE

DMTA

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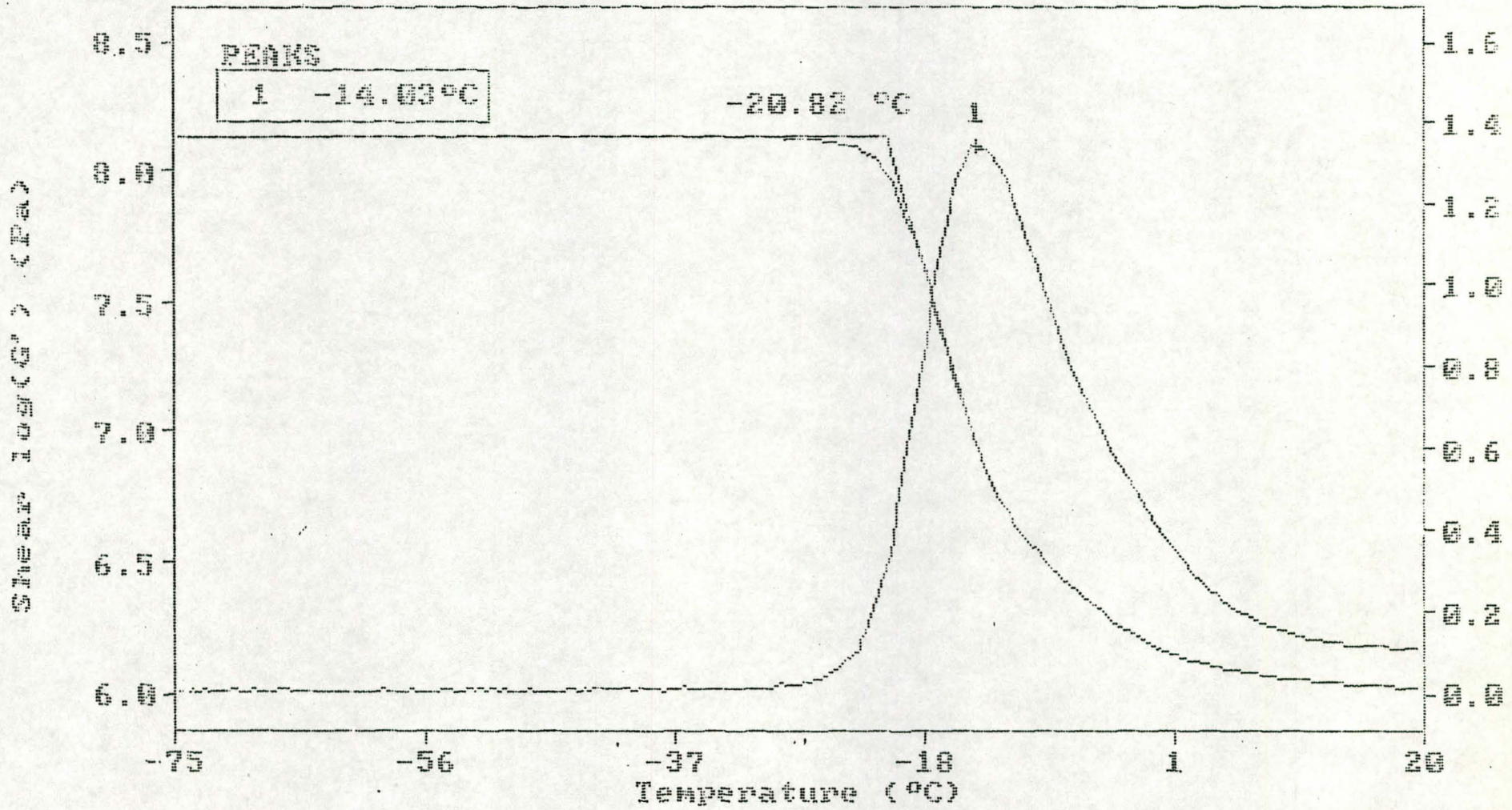

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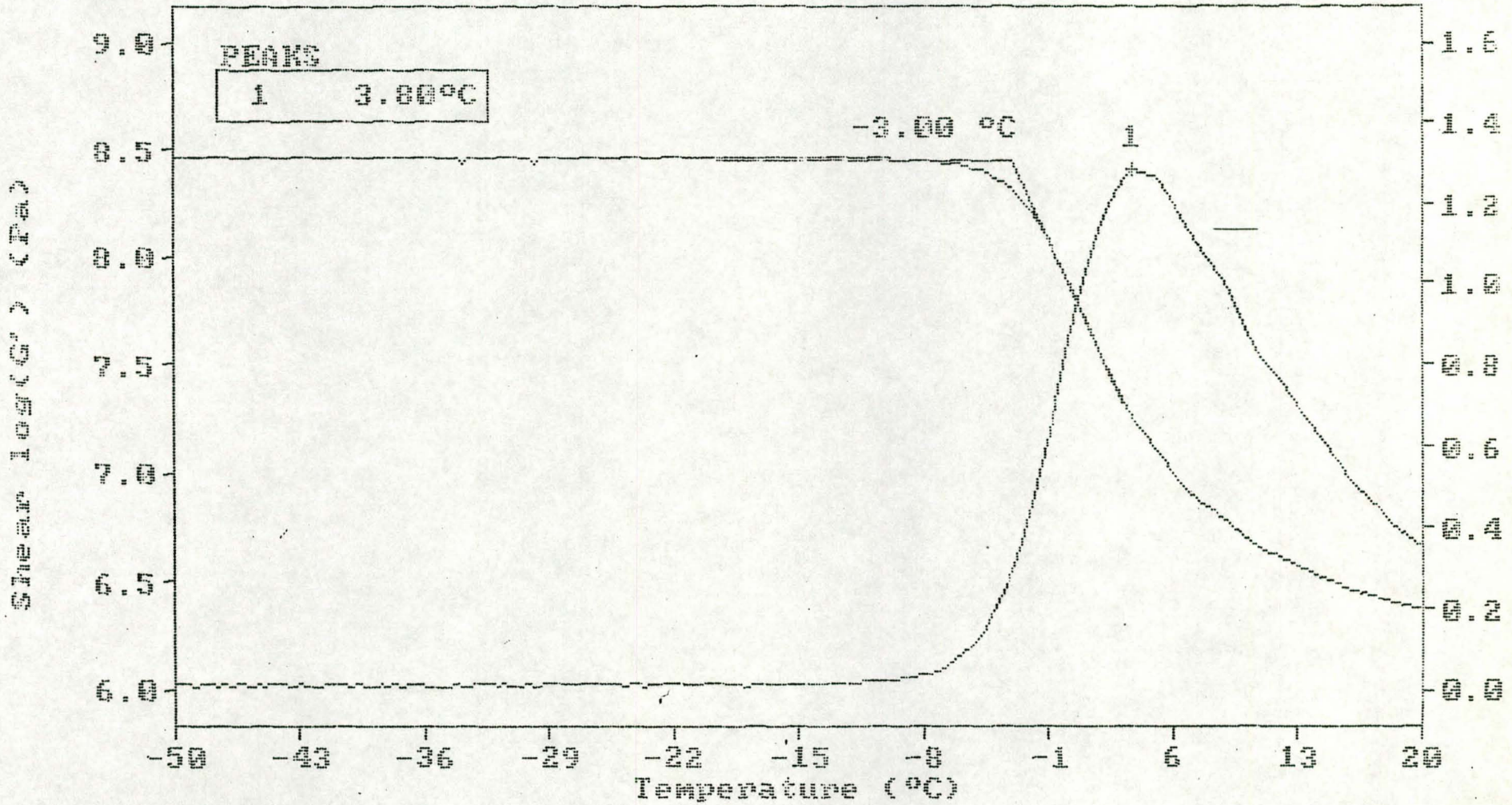

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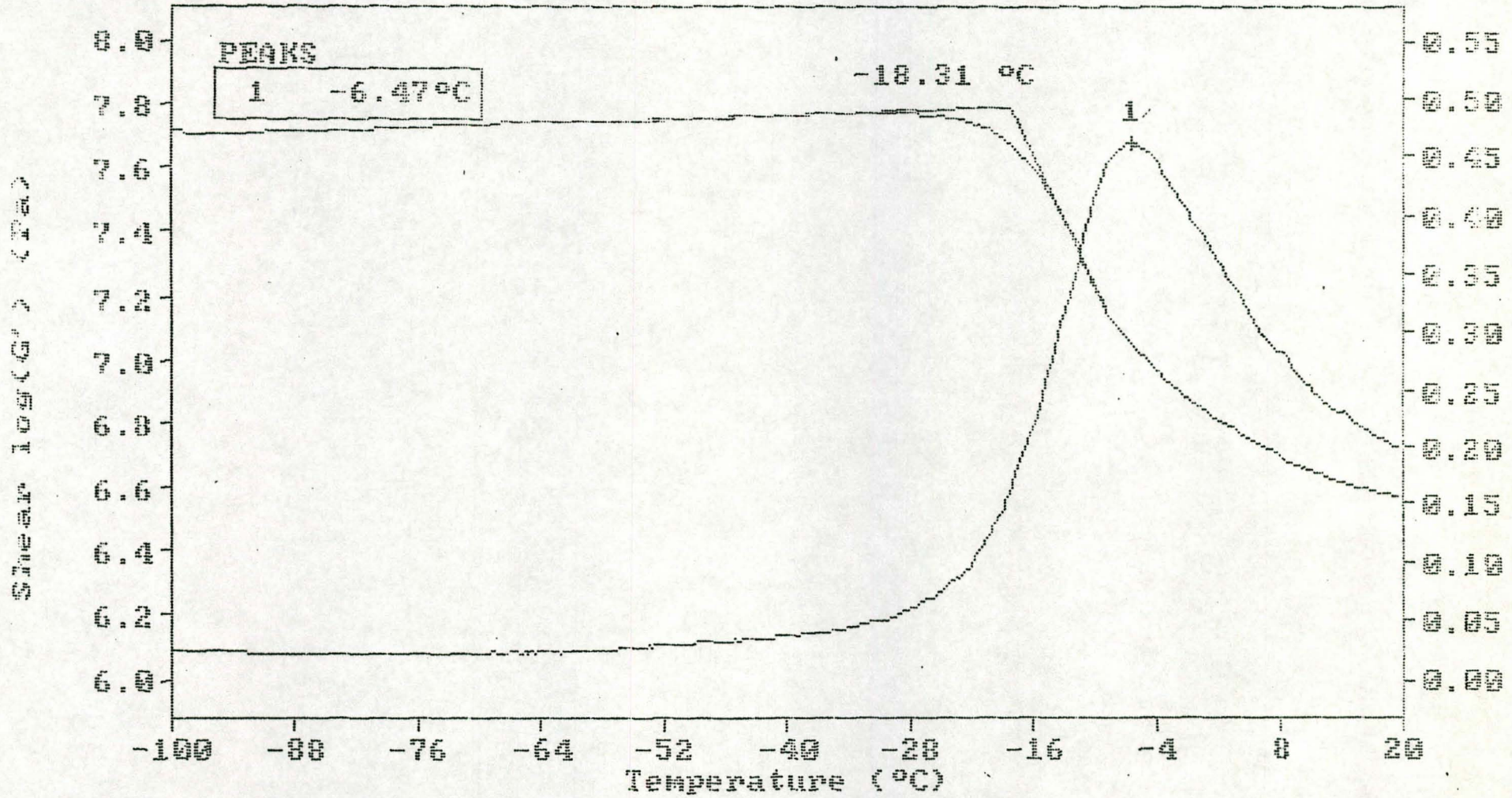

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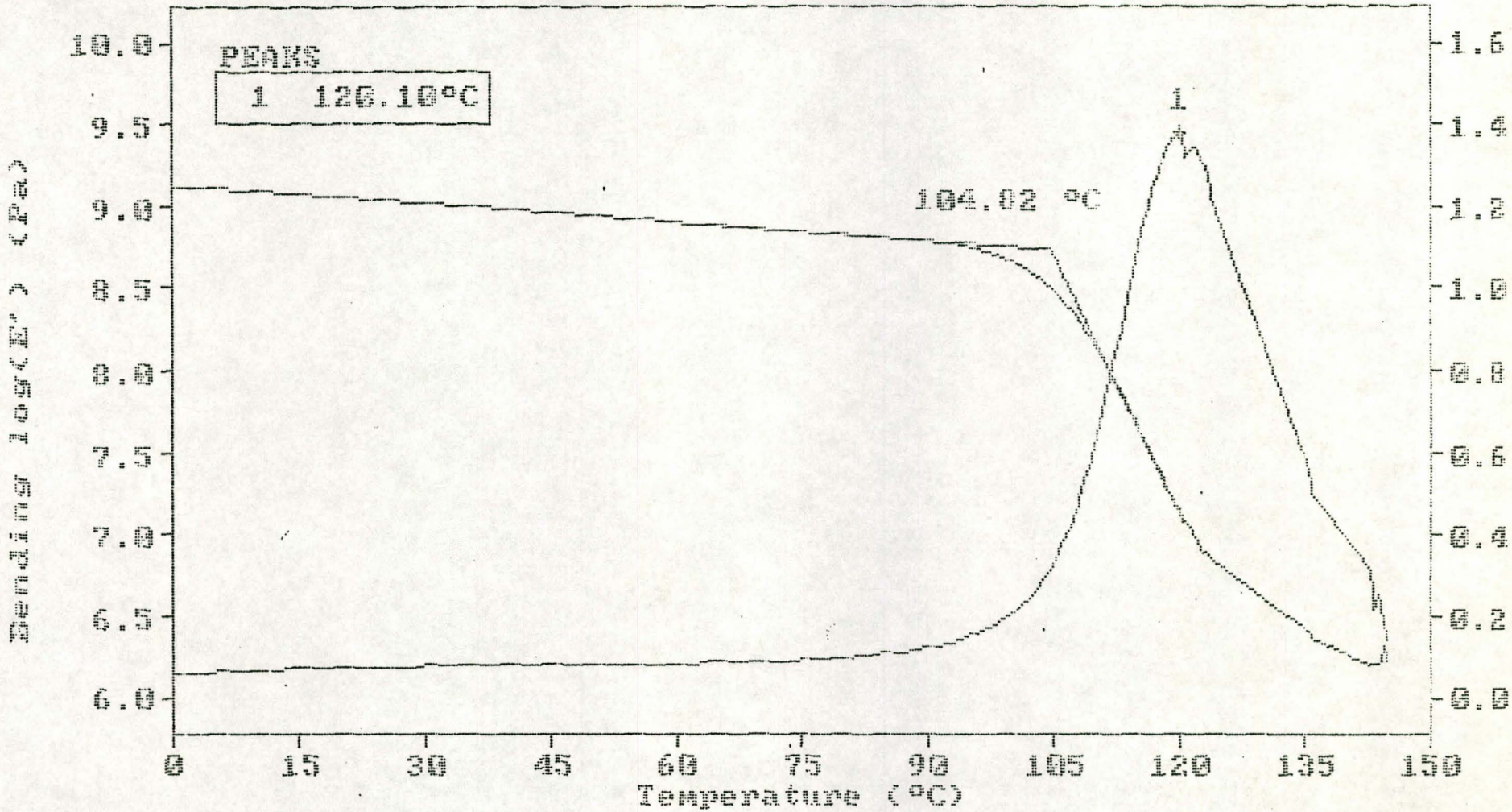

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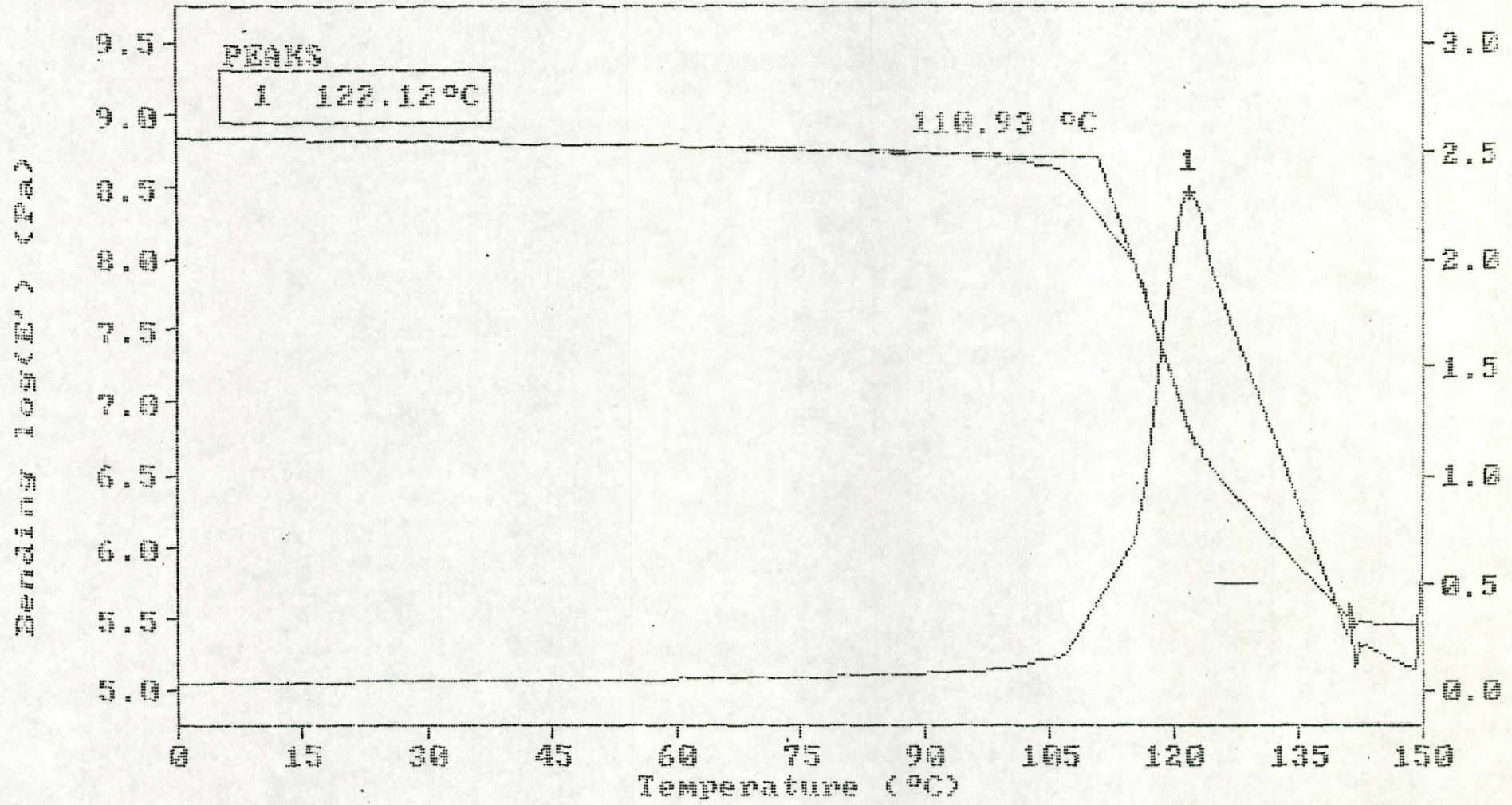

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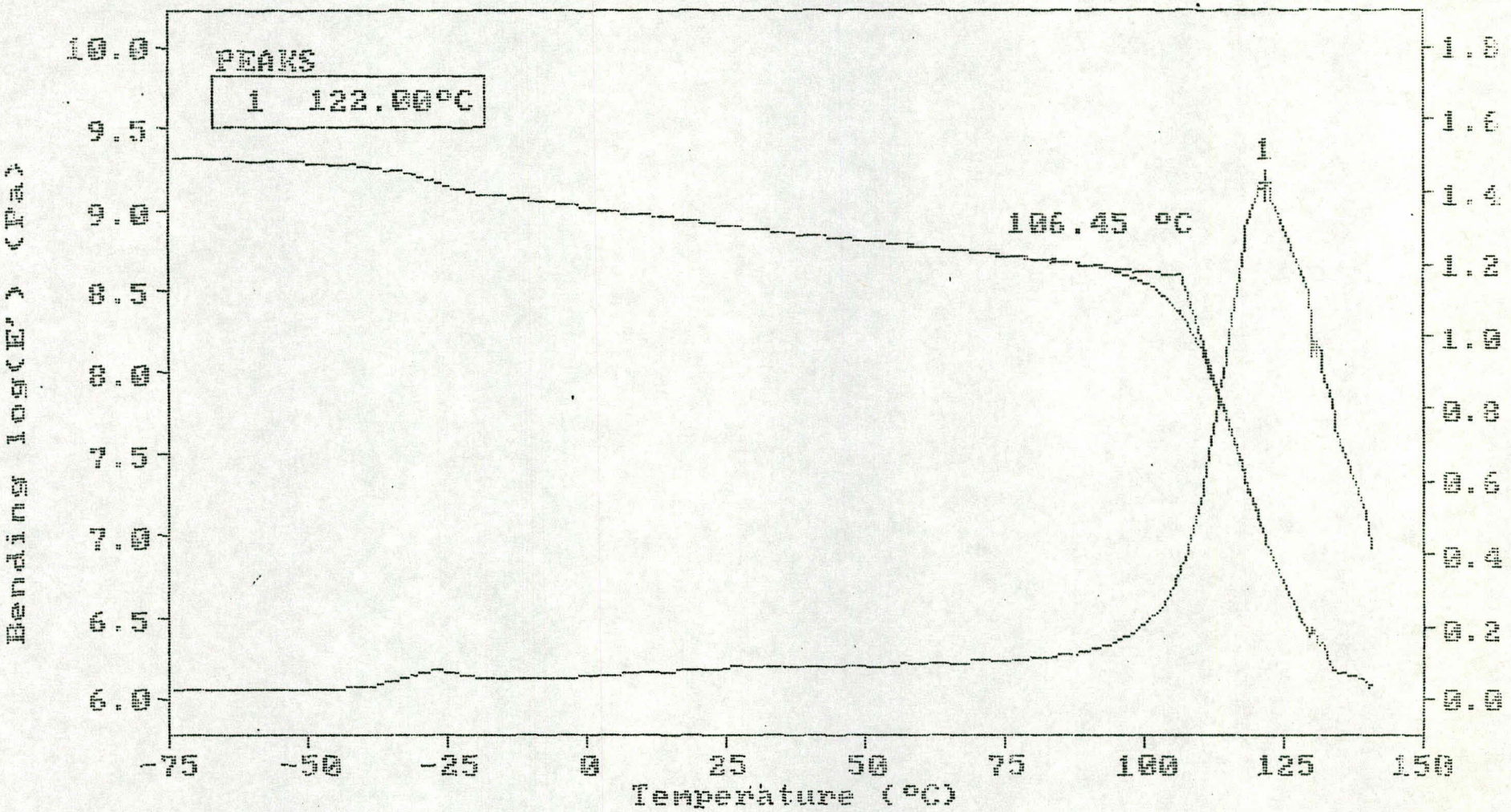

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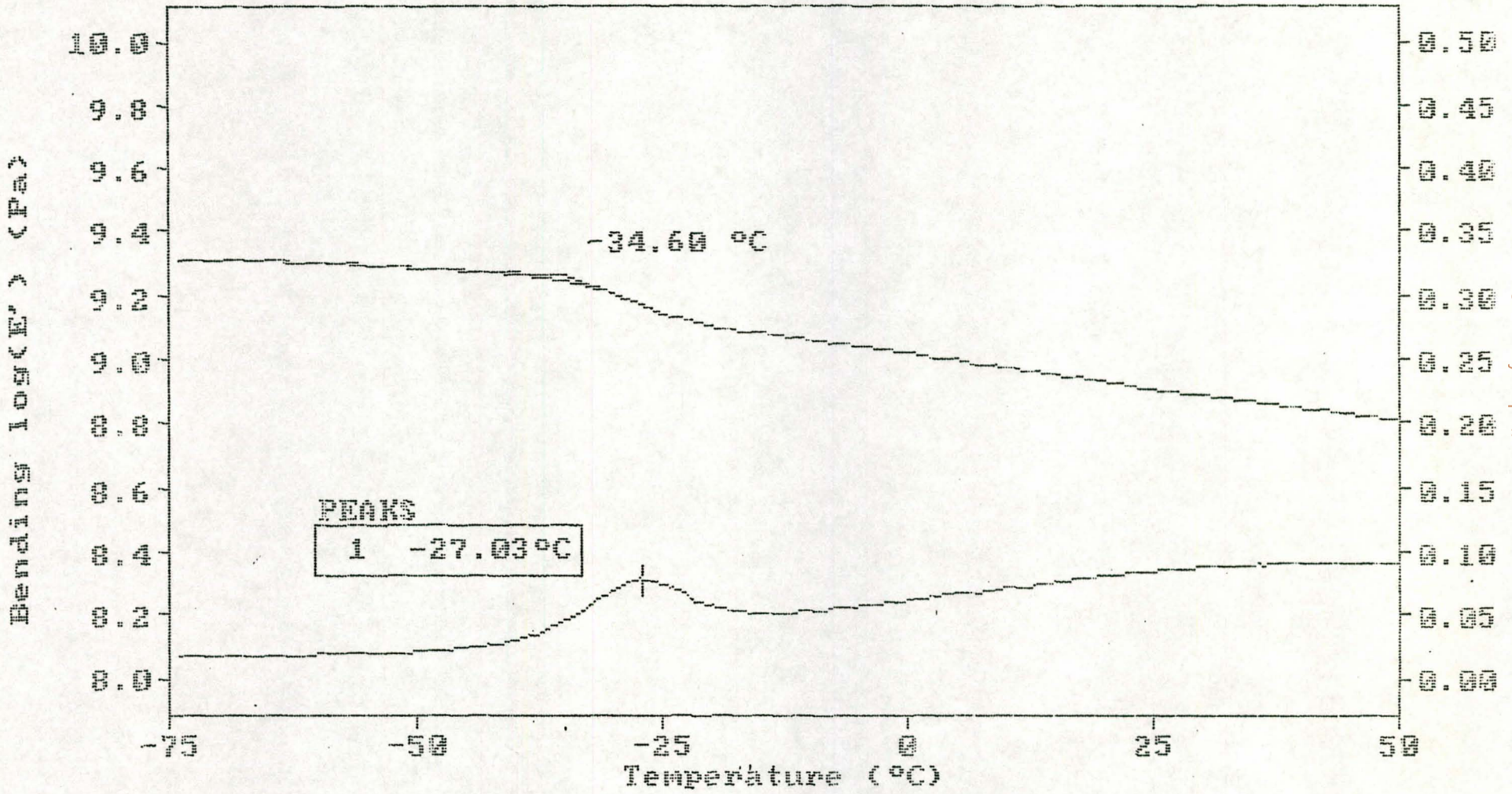

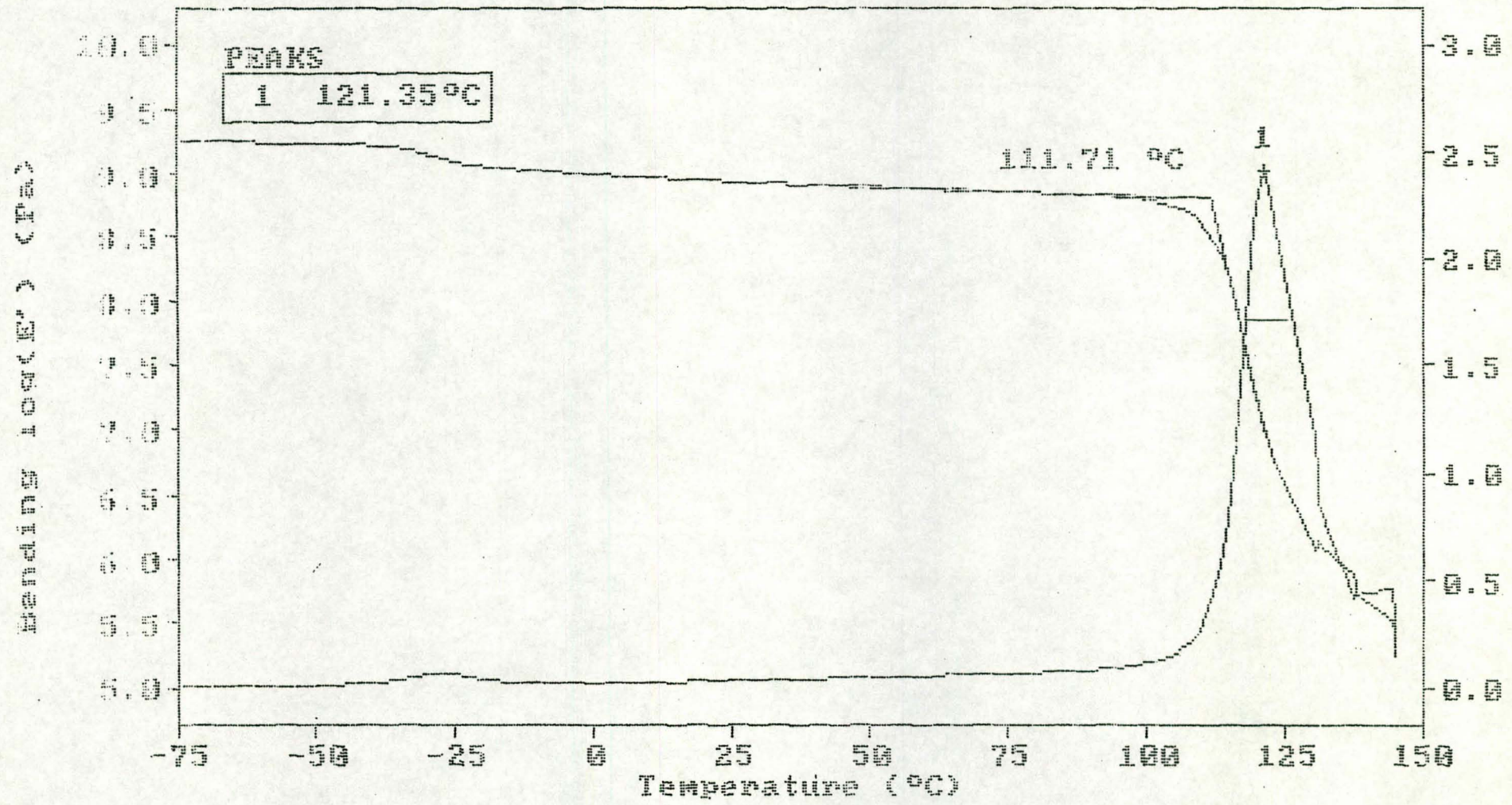

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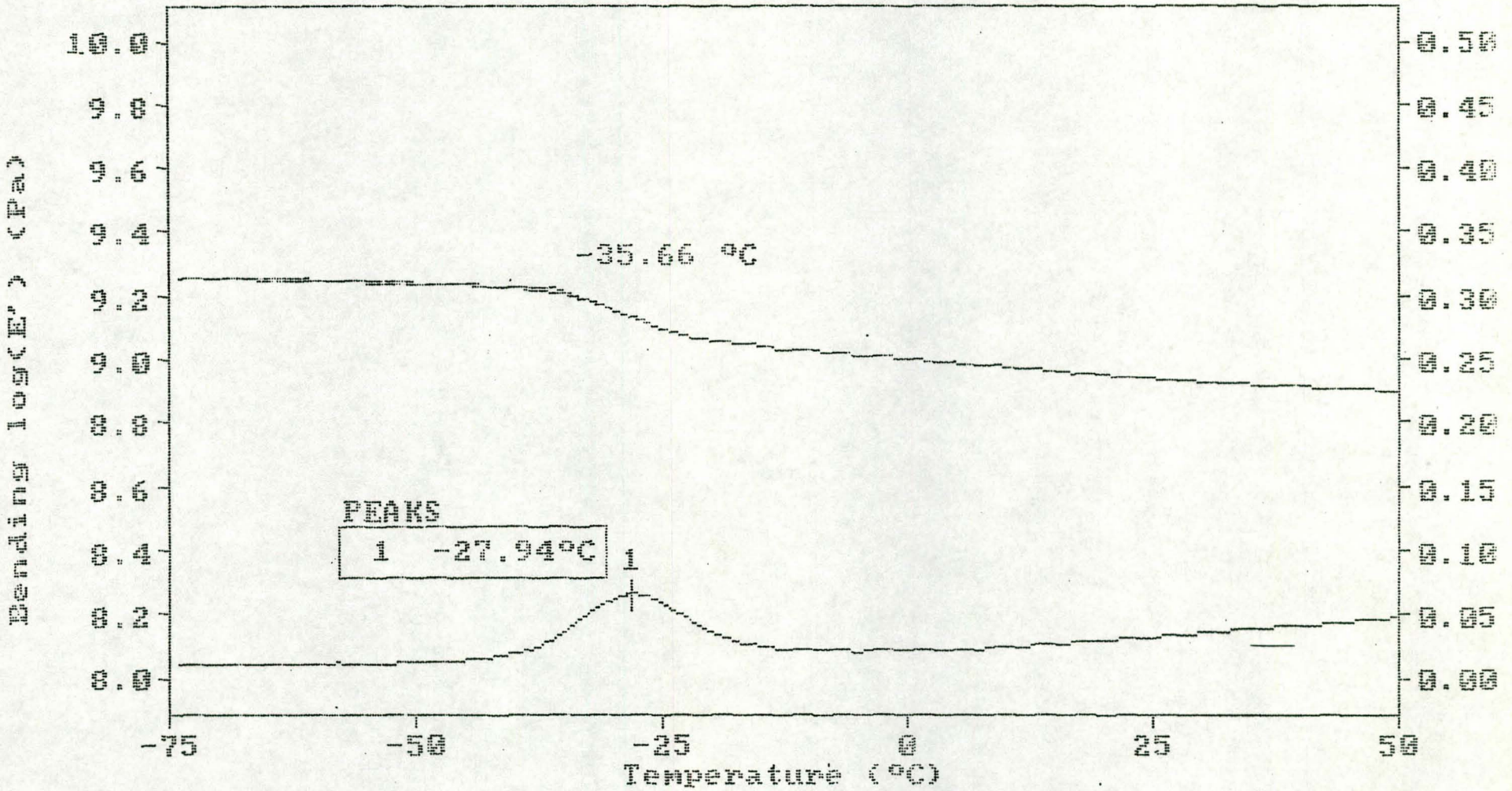

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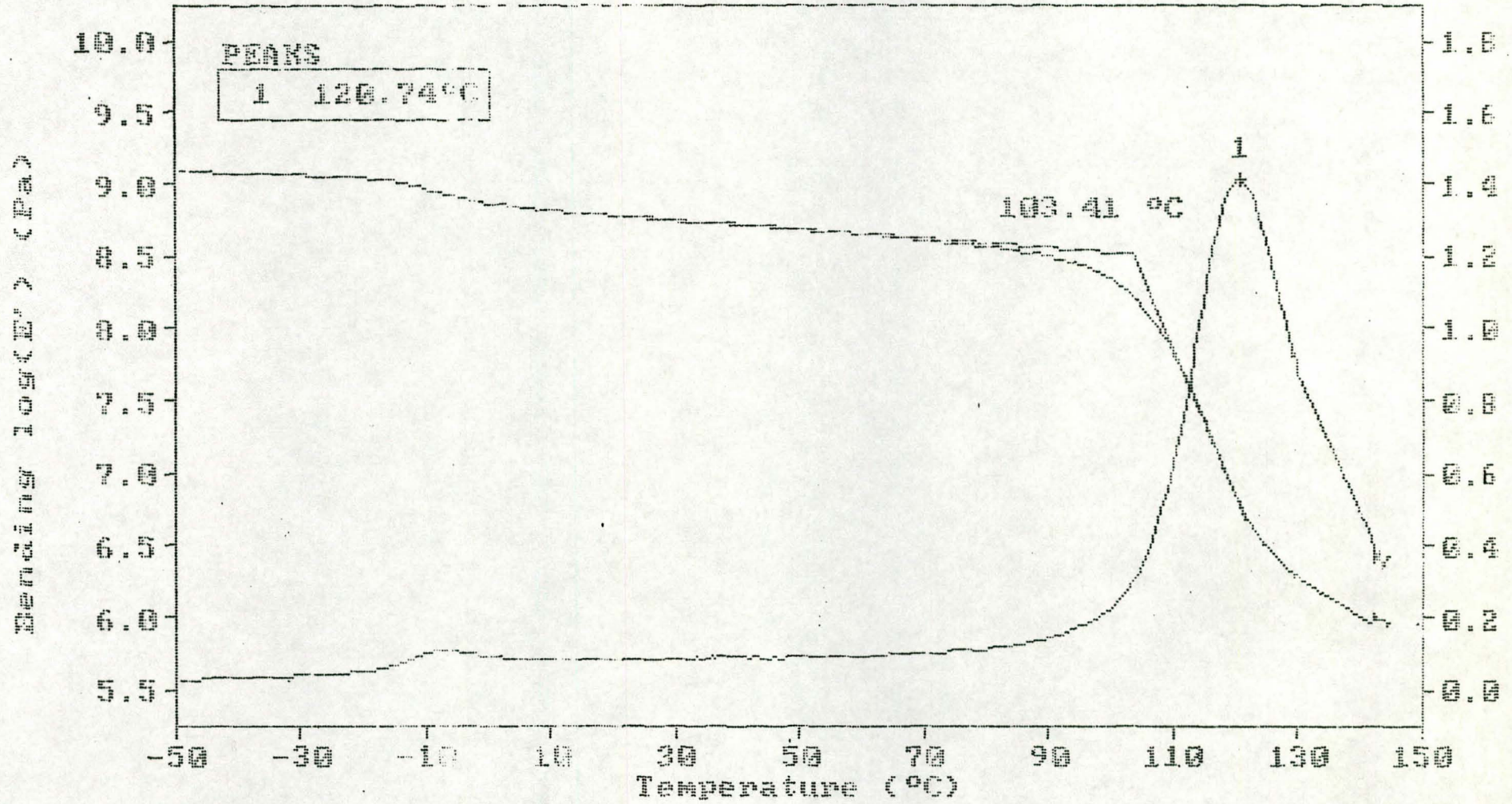

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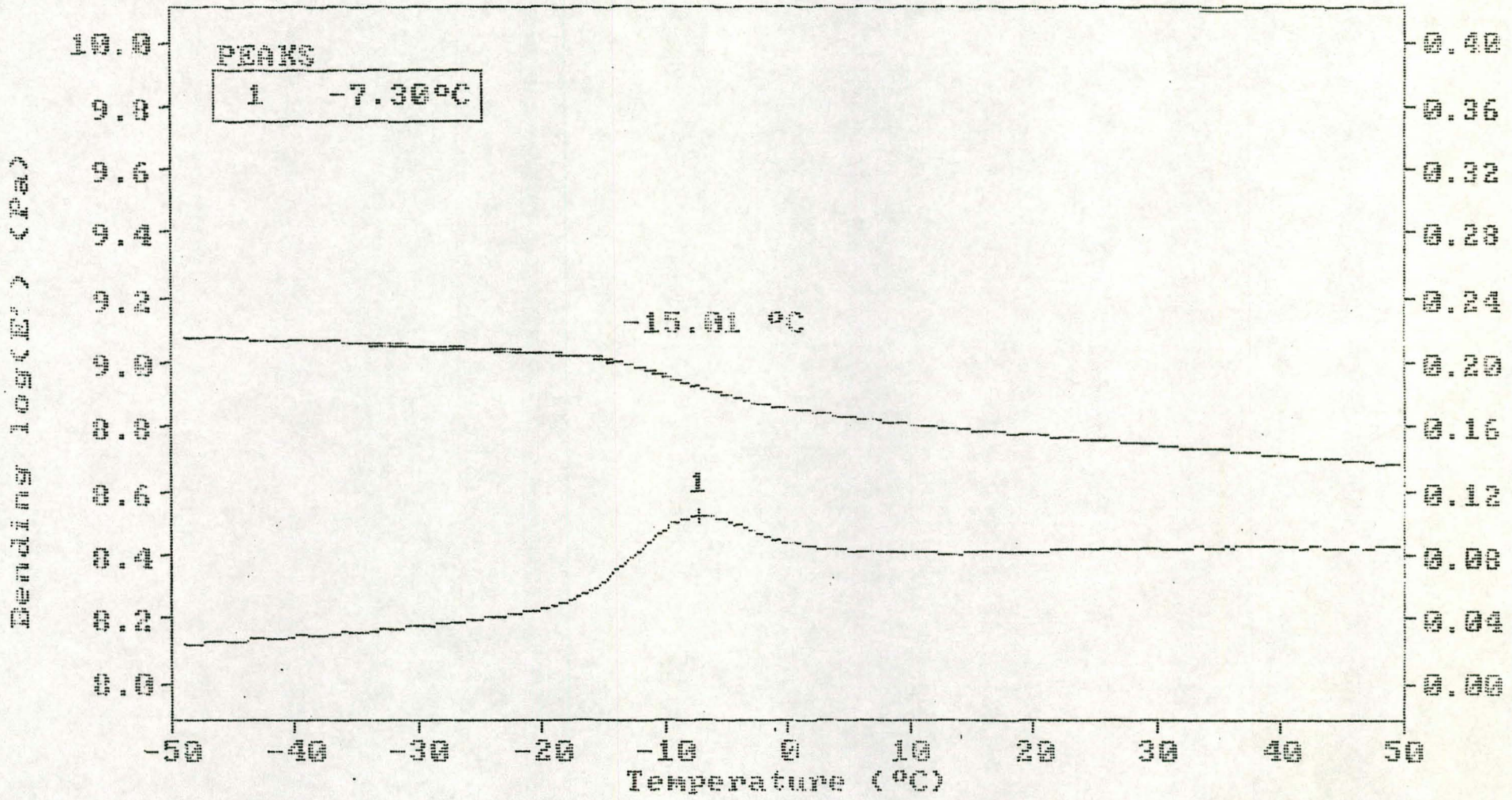

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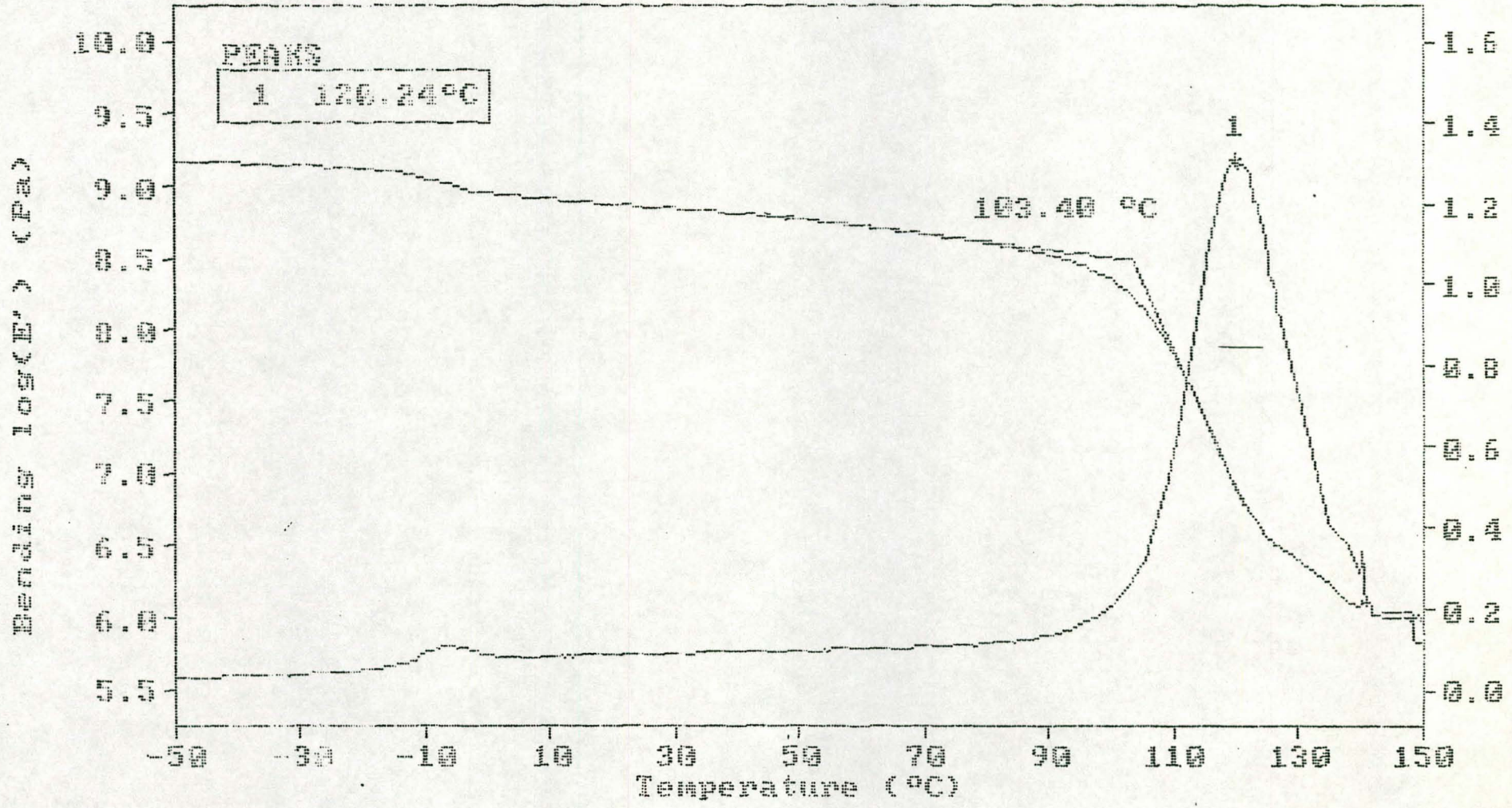

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FILENAME: C-071-6J B
OPERATOR: A MYBURGH

DATE RUN: Aug/07/1996
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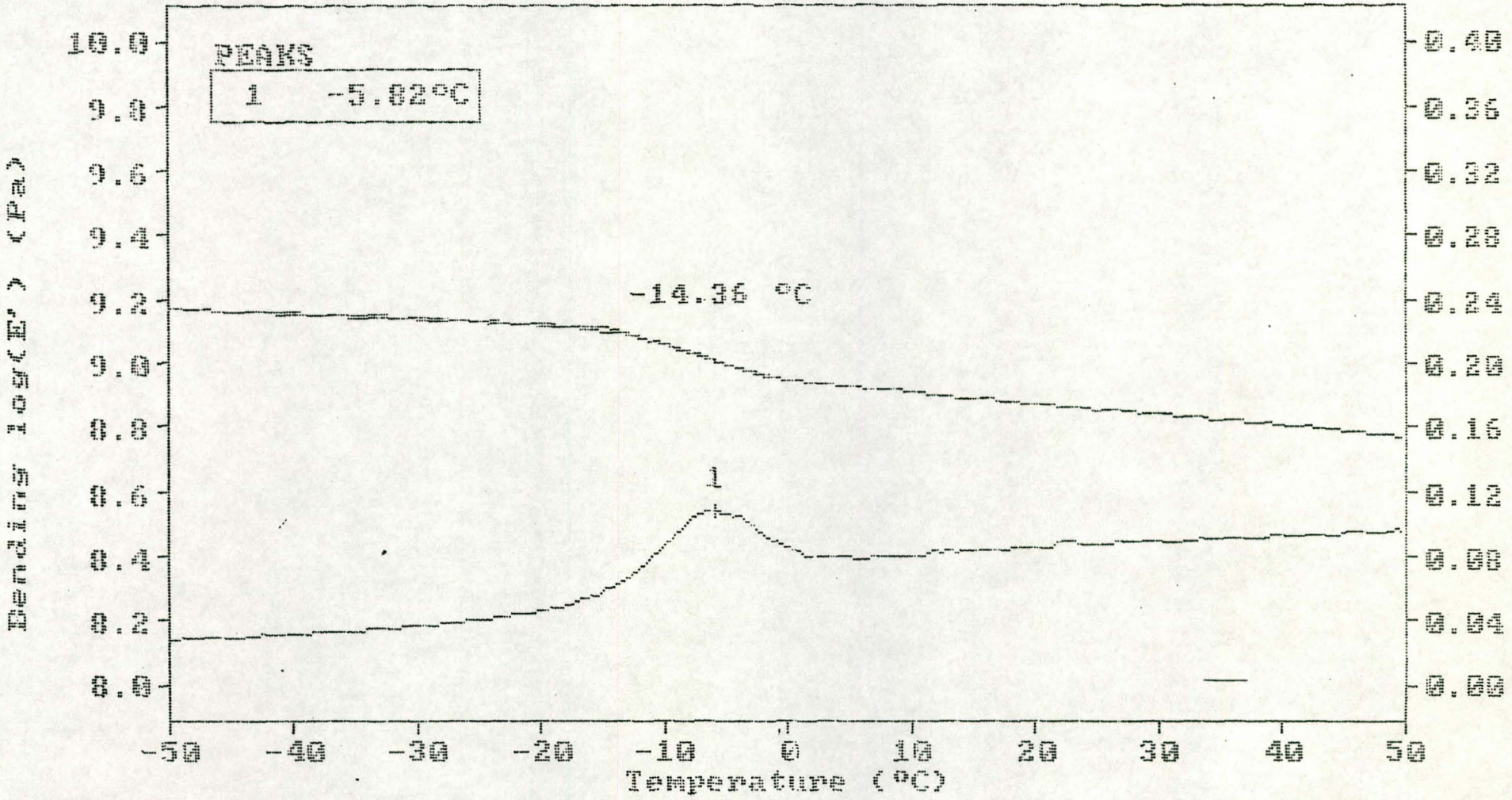

DMTA

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SUBTITLE: A3
FILENAME: G-071-6J J
OPERATOR: A MYBURGH

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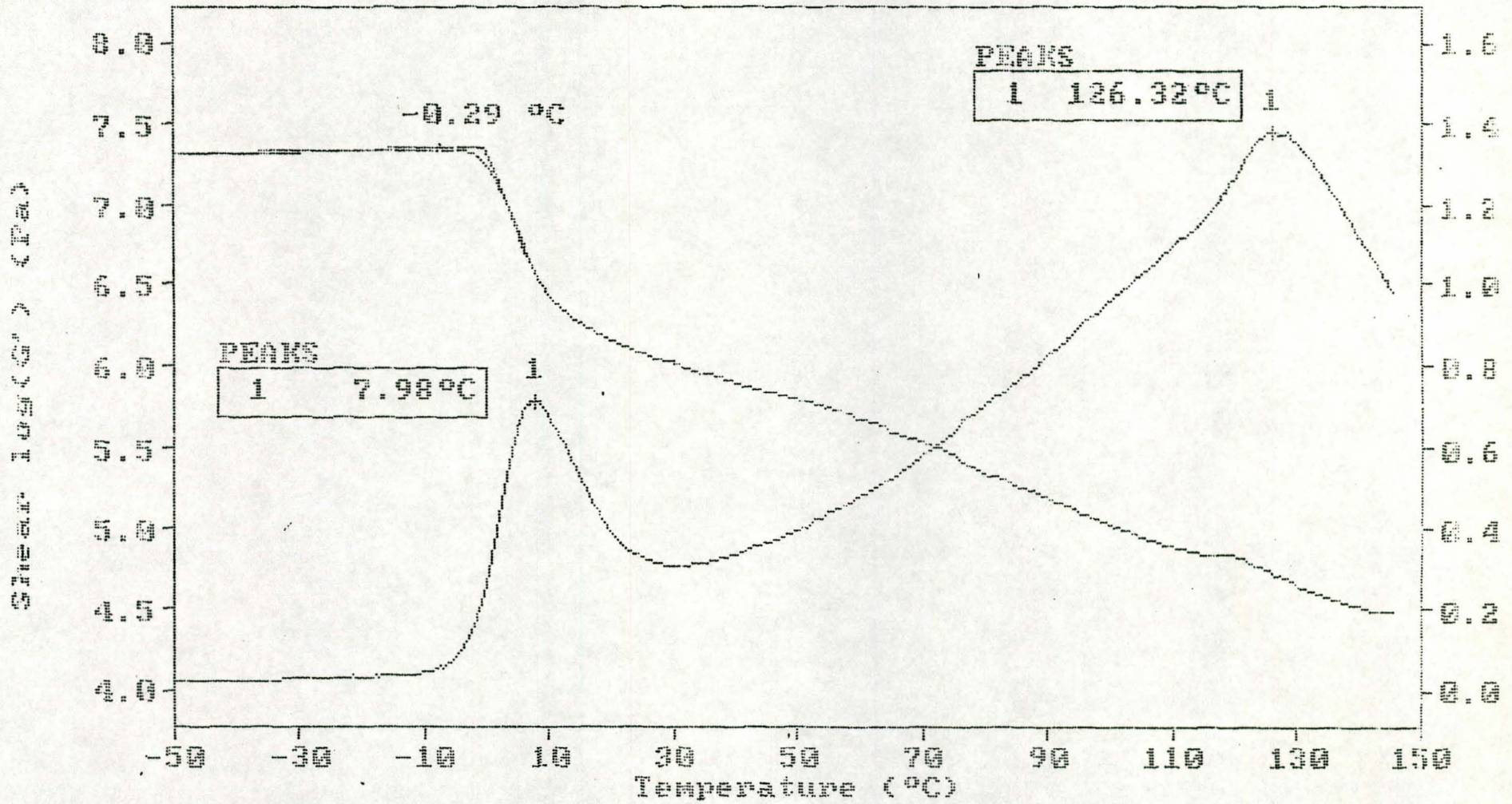

DMTA

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TITLE : ENR50/PMMA 50%
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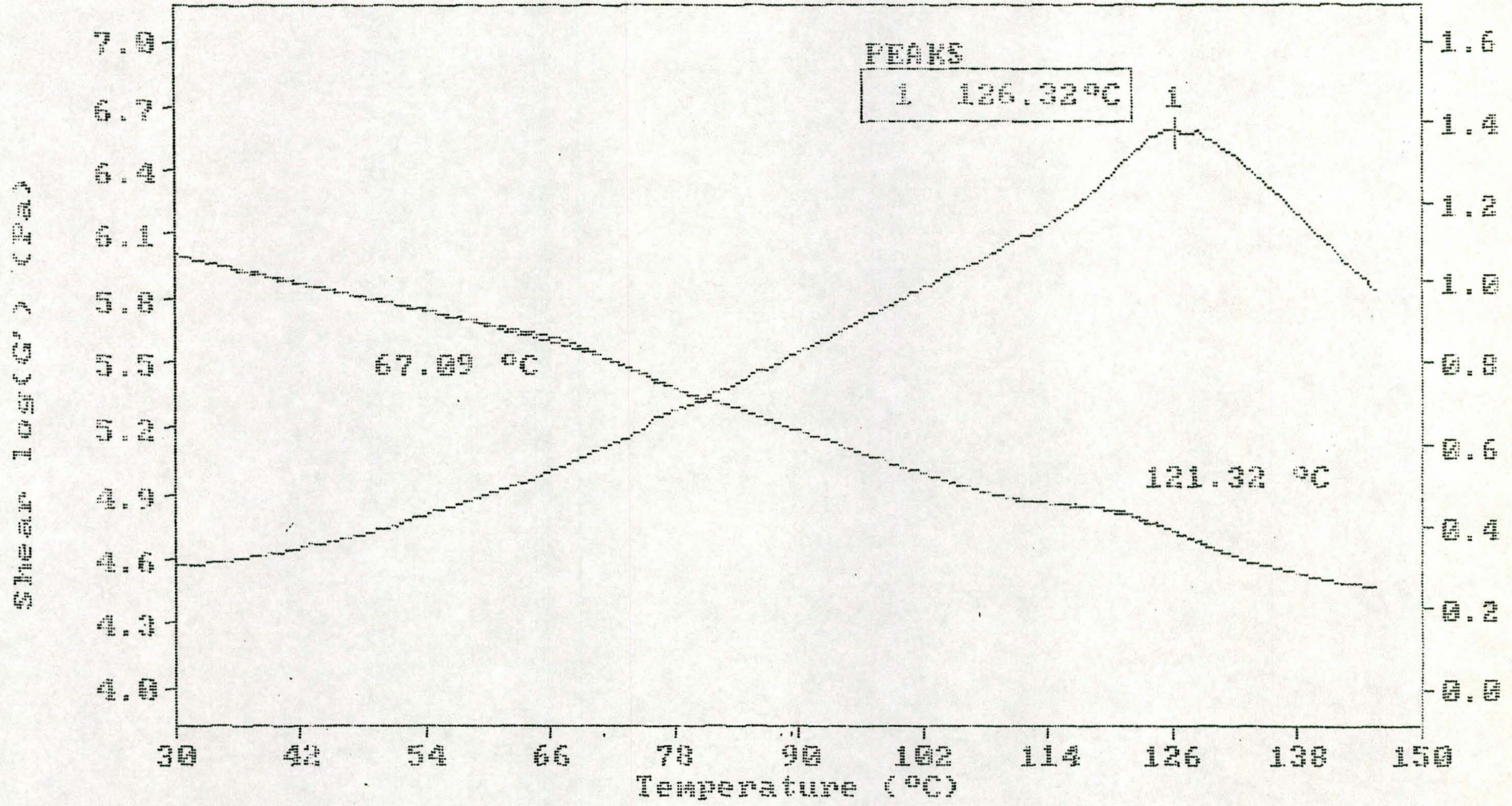

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TITLE : ENR50/PS 20%
SUBTITLE: A4
FILENAME: G-071-6J C
OPERATOR: A MYBURGH

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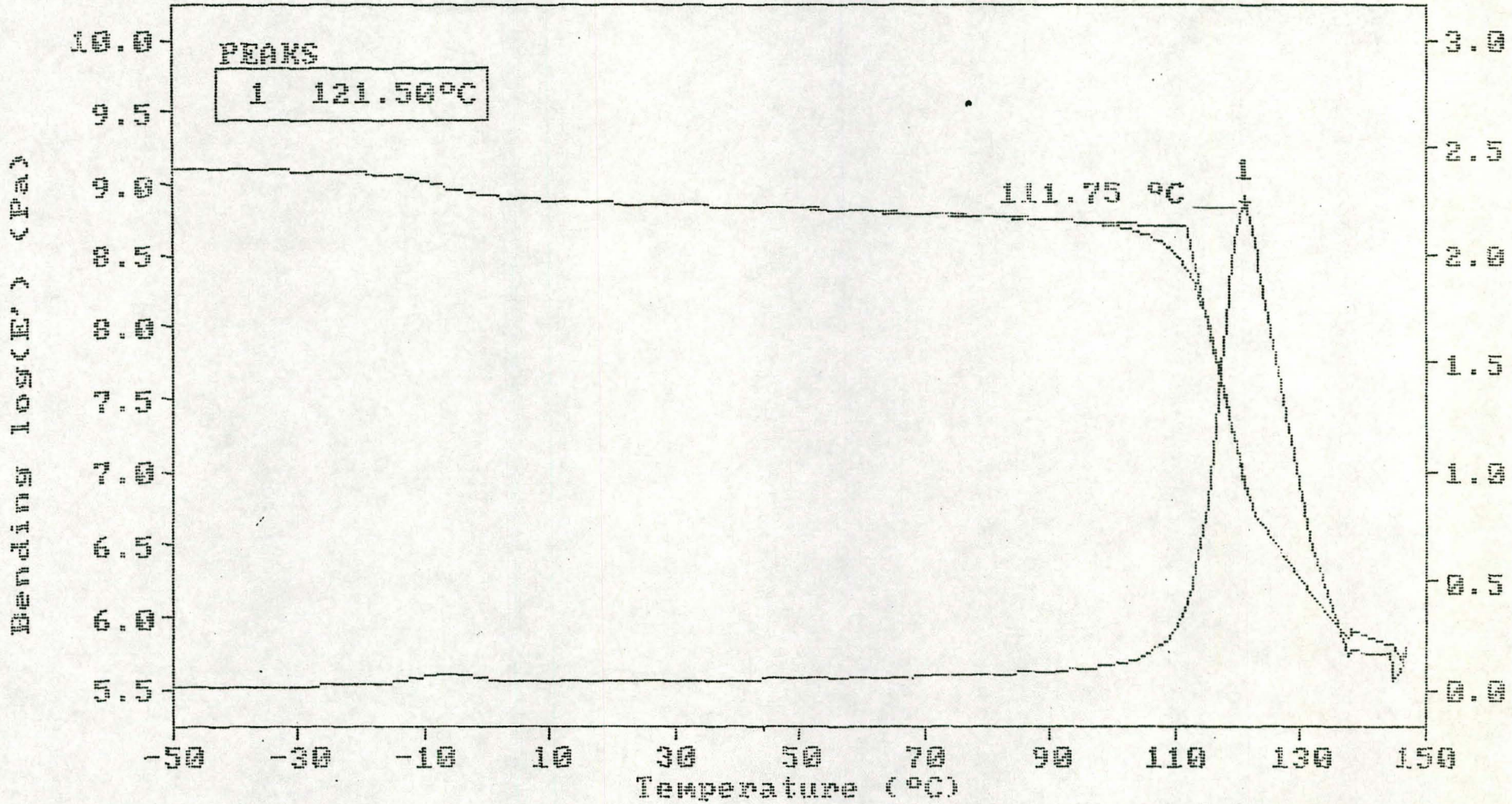

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OPERATOR: A MYBURGH

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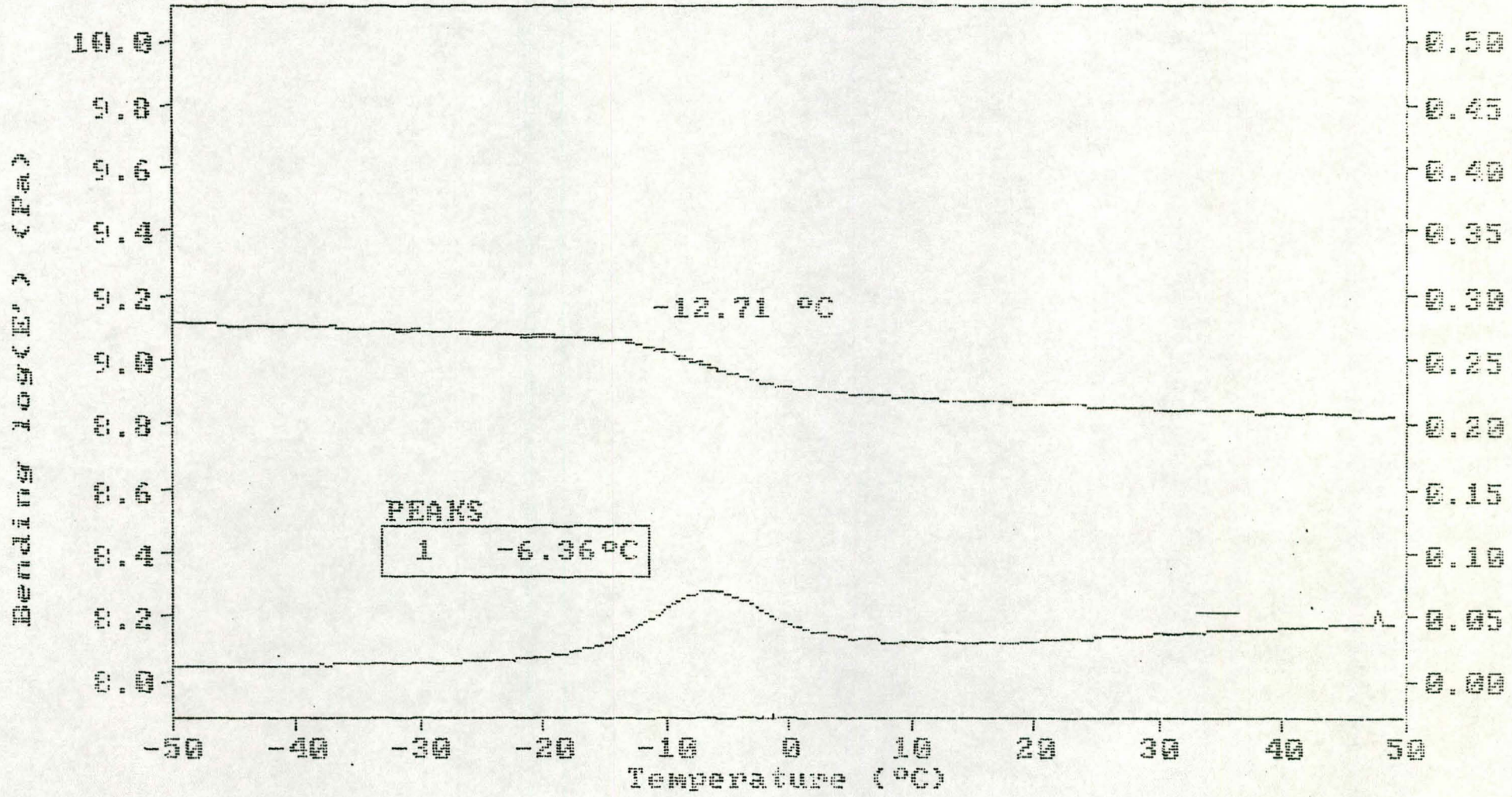

DMTA

Head: Power 300°C

TITLE : TPENR/PMMA 20%
SUBTITLE: C1
FILENAME: G-071-6J F
OPERATOR: A MYBURGH

DATE RUN: Aug/08/1996
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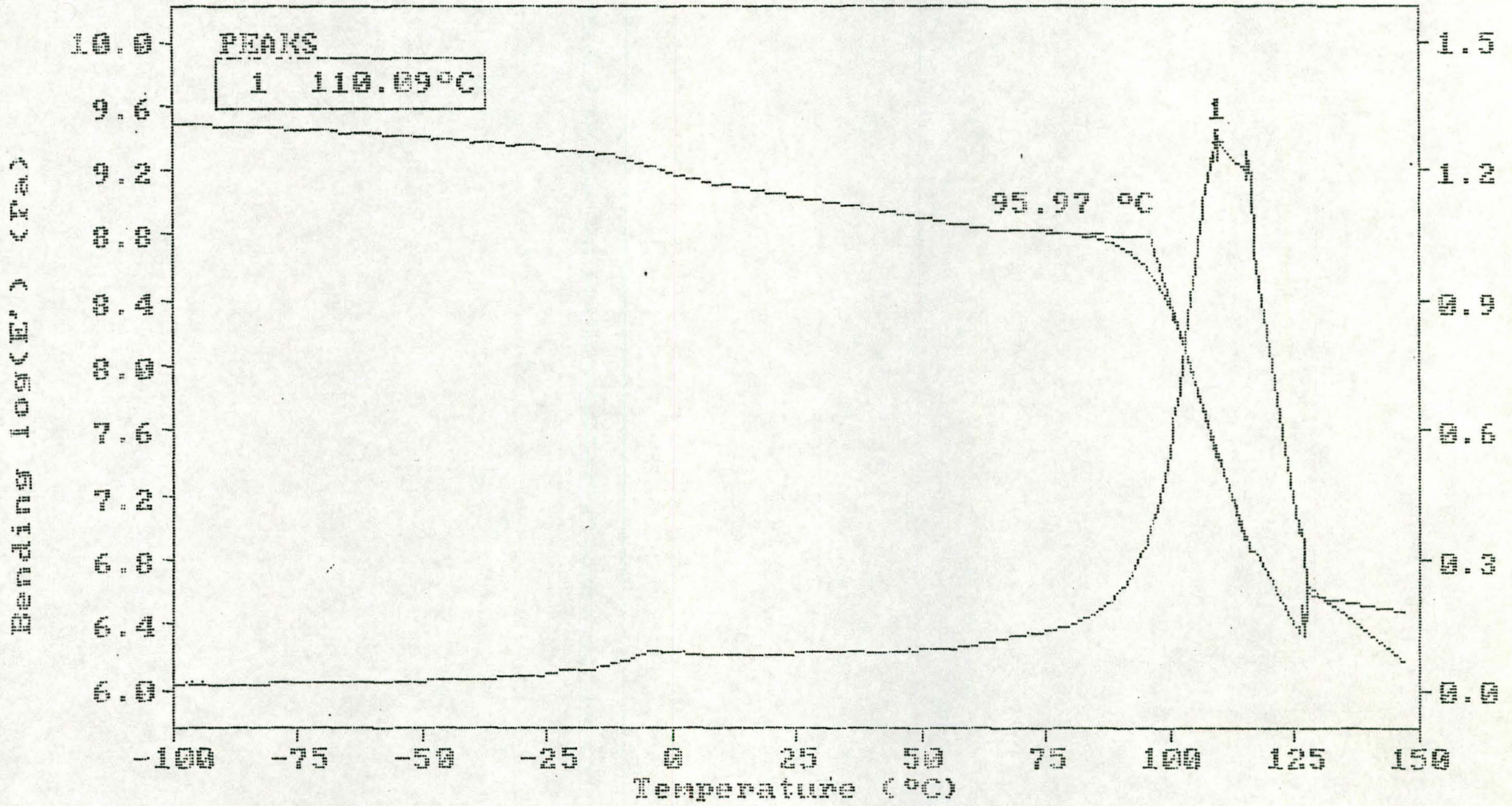

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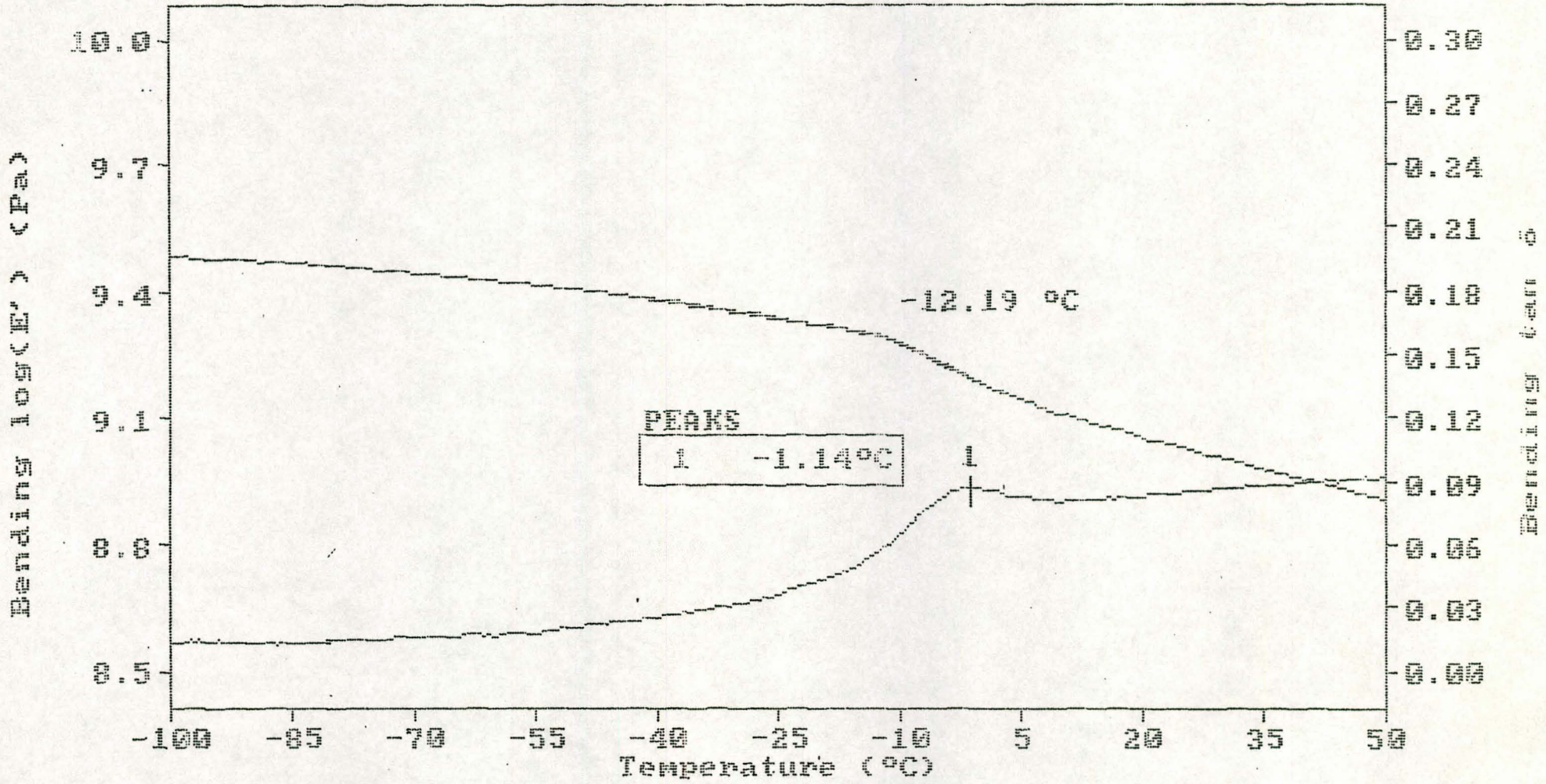

DMTA

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TITLE : TPENR/PS 20%
SUBTITLE: C2
FILENAME: G-071-6J G
OPERATOR: A MYBURGH

DATE RUN: Aug/12/1996
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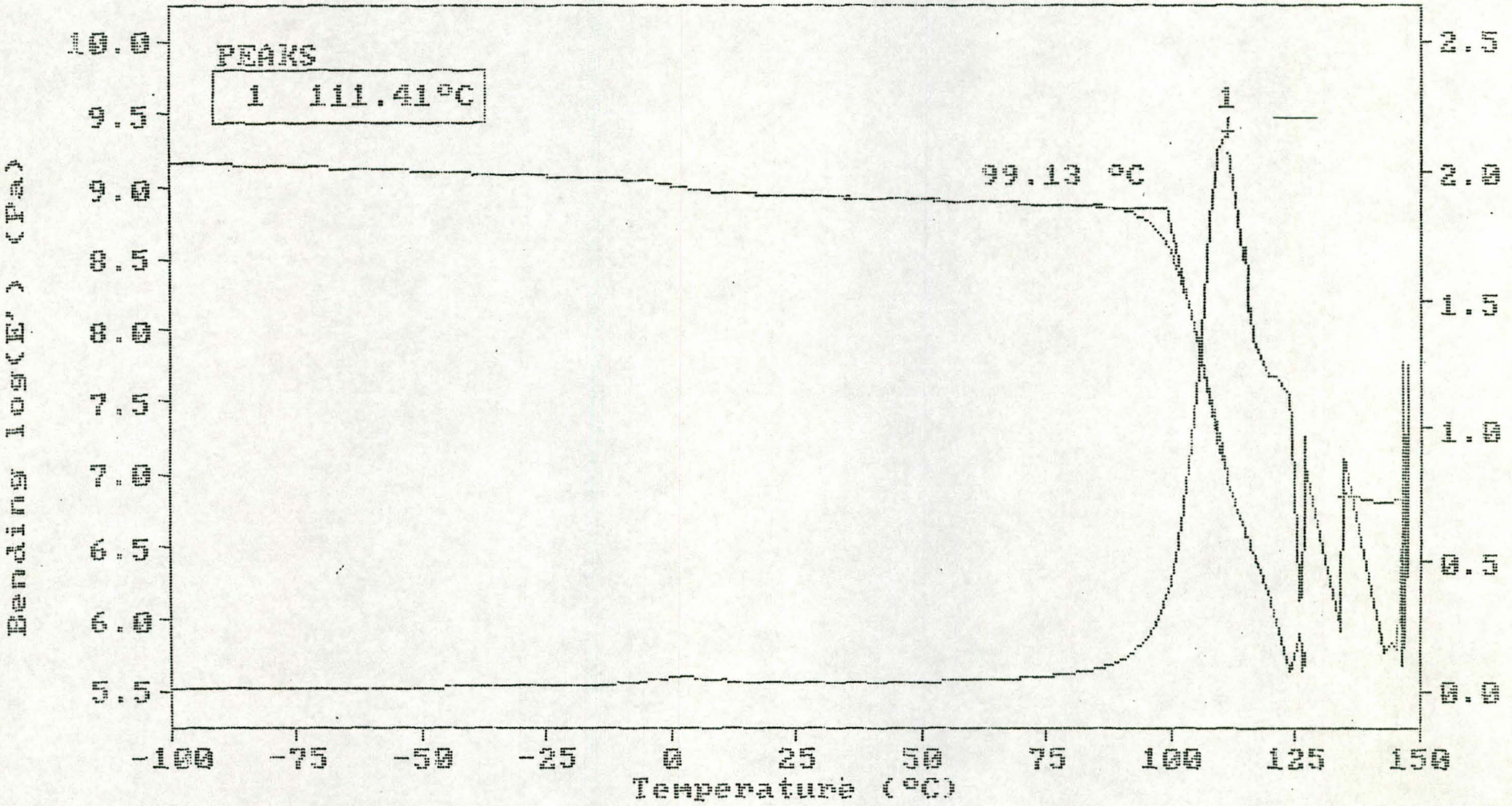

DMTA

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SUBTITLE: C2
FILENAME: G-071-6J G
OPERATOR: A MYBURGH

DATE RUN: Aug/12/1996
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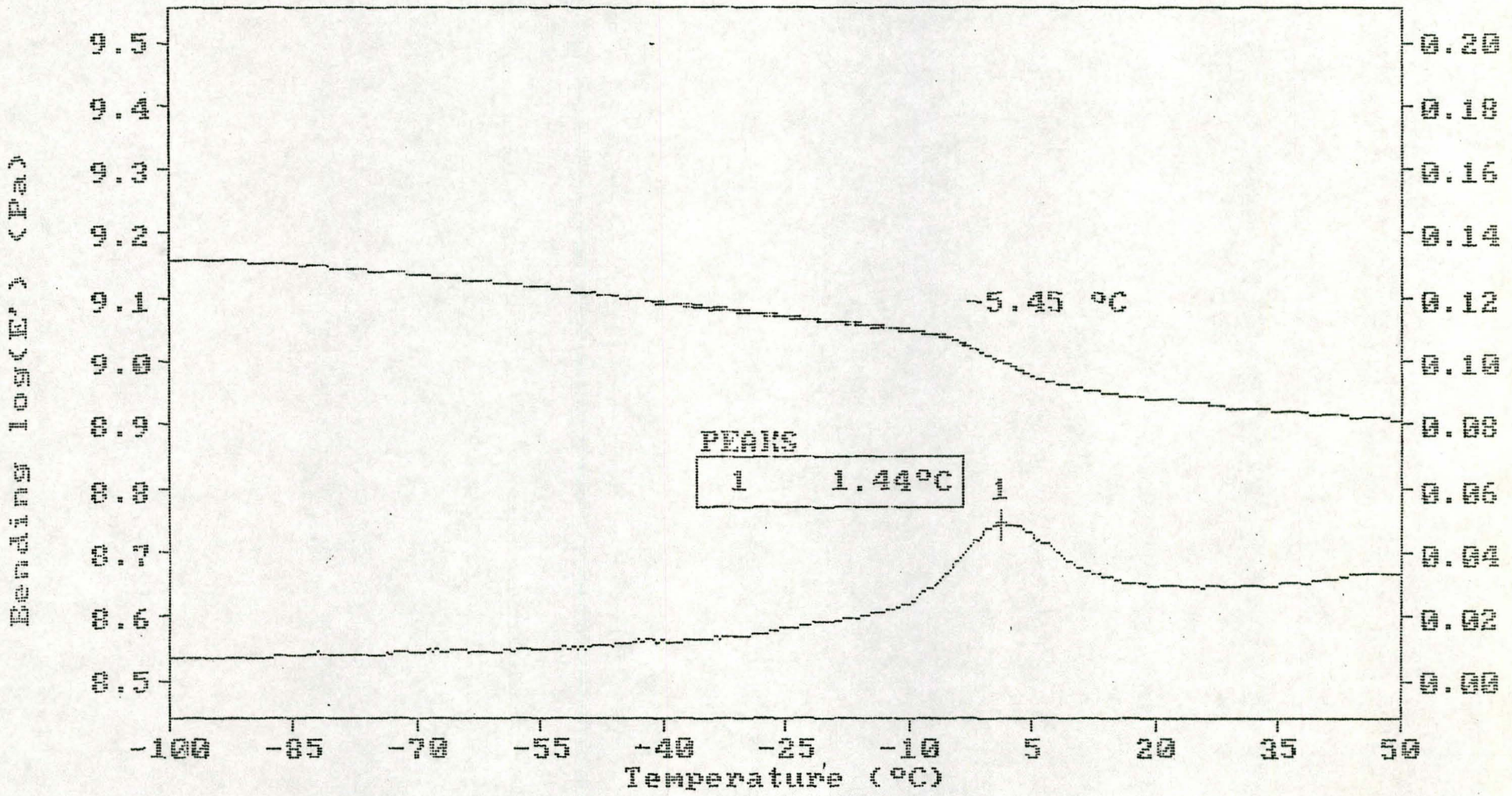


APPENDIX 2

PARTICLE SIZE DISTRIBUTIONS

MALVERN ZETASIZER

Size Report

Measurement number 3

Sample

Record Number:	4
Filename:	170298.sz2
File Path:	C:\JERRIE
Sample RI:	1.60, Abs:0.00
Dispersant RI:	1.33
Disp. Viscosity (cP):	0.794
Date (DMY):	18/02/98
Time:	13:38:46

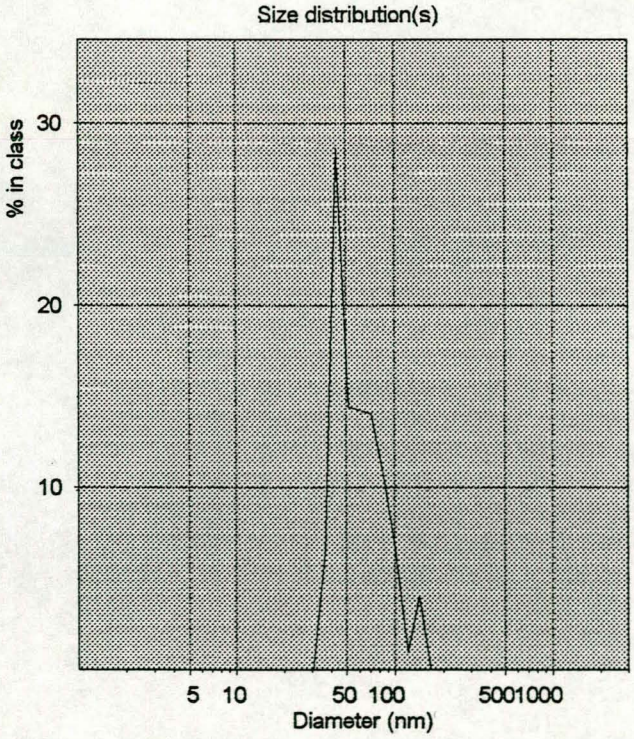
System

Instrument Type:	Zetasizer 5000
Temperature (°C):	30.2
Count rate (kCps):	625.5
Cell Type:	ZET5110
Detector Angle (deg.):	90.00
Wavelength (nm):	633.0

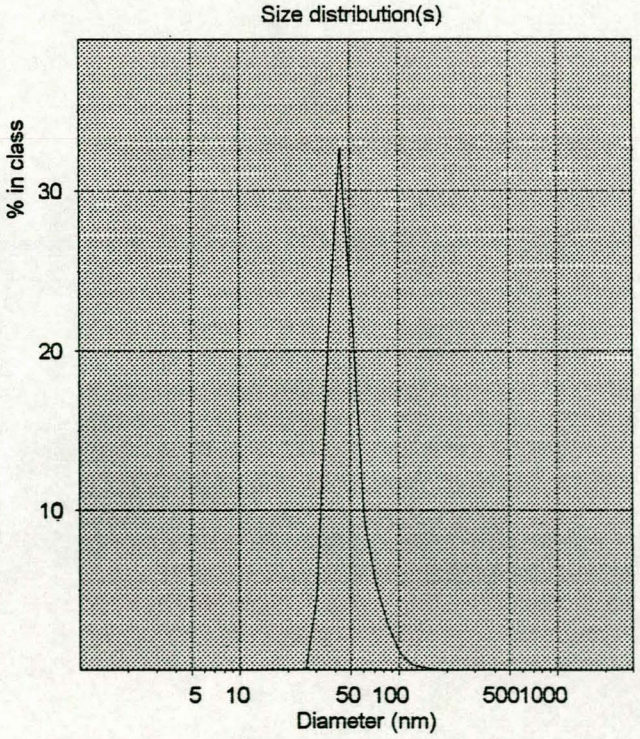
Result

Quality Factor:	Fail
Z Average Mean(nm):	55.8
Polydispersity:	0.14
Intensity Mean (nm):	63.5
Volume Mean (nm):	48.5
Analysis Mode:	Exponential

Intensity



Volume



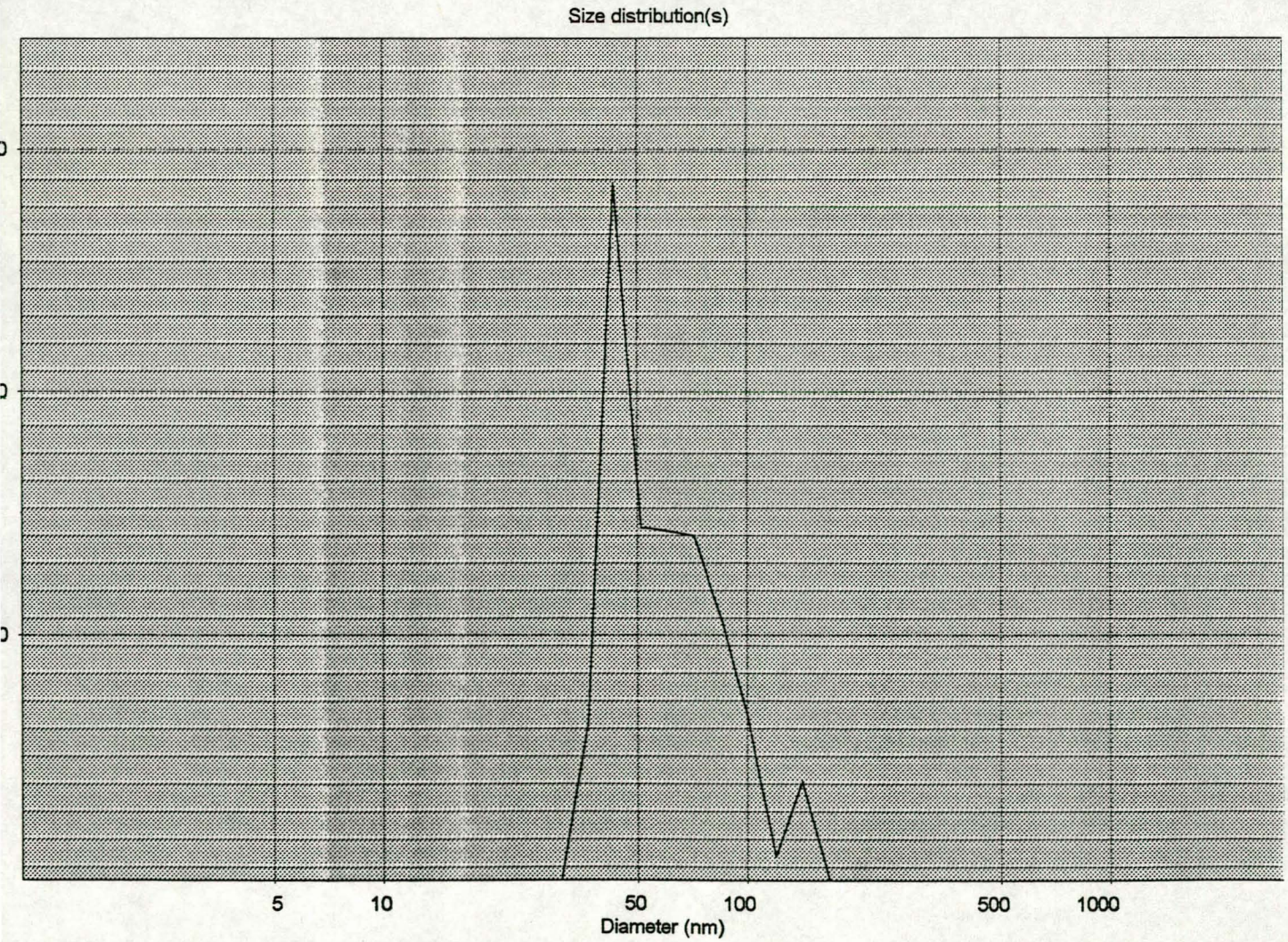
rement number 3
ta from C:\JERRIE\170298.sz2 Record 4
pe AZ110

(nm)	Intensity	Volume	Number
	0.0	0.0	0.0
	0.0	0.0	0.0
1	0.0	0.0	0.0
1	0.0	0.0	0.0
6	0.0	0.0	0.0
5	0.0	0.0	0.0
9	0.0	0.0	0.0
9	0.0	0.0	0.0
7	0.0	4.6	8.2
4	6.5	21.3	29.5
2	28.6	32.7	36.8
2	14.4	21.9	18.8
7	14.2	9.5	4.4
0	14.1	5.5	1.6
3	10.6	2.8	0.5
1.1	6.6	1.1	0.1
9.9	1.0	0.3	0.0
2.1	4.0	0.1	0.0
3.4	0.0	0.1	0.0
9.7	0.0	0.0	0.0
6.7	0.0	0.0	0.0
0.5	0.0	0.0	0.0
2.6	0.0	0.0	0.0
4.2	0.0	0.0	0.0

Peak Analysis by intensity			
Peak	Area	Mean	Width
1	95.0	60.2	18.7
2	5.0	137.7	27.8

Peak Analysis by volume			
Peak	Area	Mean	Width
1	100.0	48.5	20.7

Peak Analysis by number			
Peak	Area	Mean	Width
1	100.0	43.2	18.0



ze(nm)	Intensity	Volume	Number
40.6	0.0	0.0	0.0
49.6	0.0	0.0	0.0
60.6	0.0	0.0	0.0
74.0	0.0	0.0	0.0
90.4	0.0	0.0	0.0
110.4	0.0	0.2	1.2
134.9	0.5	1.3	6.0
164.8	4.6	8.1	20.5
201.3	40.5	16.2	31.6
245.9	25.9	15.1	21.1
300.5	15.4	12.3	8.1
367.1	9.6	18.6	5.7
448.4	3.5	20.2	4.3
547.8	0.0	8.1	1.5
669.3	0.0	0.0	0.0
817.6	0.0	0.0	0.0
998.9	0.0	0.0	0.0
1220.3	0.0	0.0	0.0
1490.8	0.0	0.0	0.0
1821.3	0.0	0.0	0.0
2225.1	0.0	0.0	0.0
2718.3	0.0	0.0	0.0
3320.9	0.0	0.0	0.0
4057.0	0.0	0.0	0.0

Peak Analysis by intensity

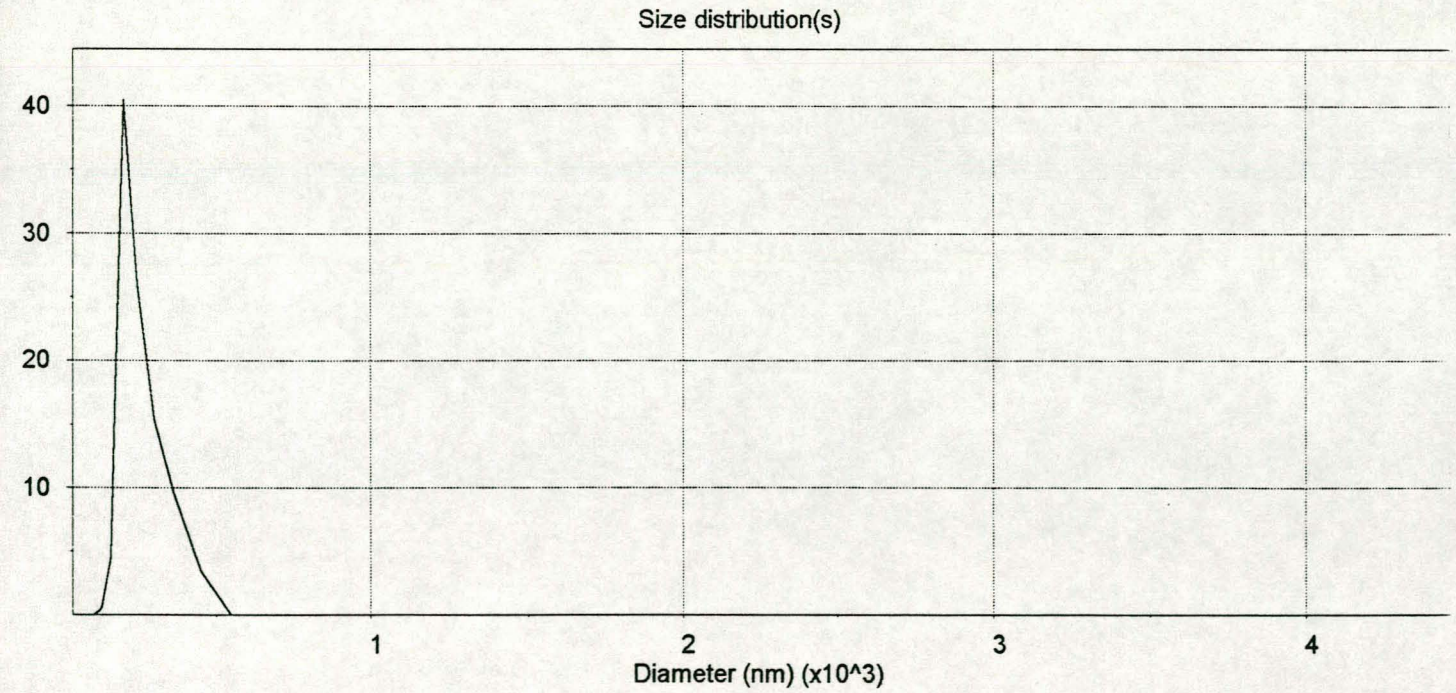
Peak	Area	Mean	Width
1	100.0	250.7	94.8

Peak Analysis by volume

Peak	Area	Mean	Width
1	47.3	229.4	81.0
2	52.7	405.6	164.1

Peak Analysis by number

Peak	Area	Mean	Width
1	100.0	231.5	113.0



cAngle	KCps	ZAve	Poly	Fit Error	Time	Function	Analysis	File	Title
90.0	682.1	405.7	1.000	0.00548	12:41:05	Intensity	Multimodal	JERRIE5	Measurement number

APPENDIX 3

DRAFT PRESENTED AS ARTICLE TO THERMOCHEMICAL ACTA (CHARACTERIZATION OF CORE-SHELL POLYMERS AND GRAFTED LATICES BY COMBINED DYNAMIC MECHANICAL / ELECTRICAL ANALYSES)

CHARACTERIZATION OF CORE-SHELL POLYMERS AND GRAFTED LATICES BY COMBINED DYNAMIC MECHANICAL / ELECTRICAL ANALYSES

R. D. SANDERSON AND J. P. VERMEULEN
Institute for Polymer Science
University of Stellenbosch, Stellenbosch, South Africa

1 INTRODUCTION

Research was done to create a thermoplastic elastomer (TPE) binder that would have the same or improved properties as those used in Low Vulnerability Ammunition (LOVA) propellants.

Such a binder can be very challenging to formulate since it must possess two basically conflicting properties. First, it must have the ability to absorb localized heat and, second it should be able to enhance the energy of the propellant by releasing oxygen [1]. The physical and thermal properties of the binder must also be suitable for proper mixing and processing of the propellant [1]. Suitable binders would therefore be thermoplastic elastomers, which will soften enough when heated for thorough mixing with the RDX, but will still maintain their toughness and rigidity in the propellant when cooled to ambient temperature.

Epoxidized Natural Rubber (ENR) was therefore used in conjunction with methyl methacrylate (MMA) to create this thermoplastic binder. ENR imparts a low glass point (T_g) and good impact resistance [2], which will resist fracture by hypervelocity impact, whereas methyl methacrylate contributes to a high T_g. Unique properties of ENR are the epoxide rings that act as a source of oxygen and steric ring strain that enhances energy. The thermoplastic binder was created by the polymerization and grafting of MMA onto ENR. The grafting sites were created on the ENR by the reaction of acrylic/methacrylic acid with the epoxide groups and the amount of acrylic/methacrylic acid was controlled, to obtain a narrow molecular weight distribution of polymerized MMA (PMMA).

The low vulnerability program (LOVA) was created to address the problem of the unintentional ignition in conventional propellants [3]. Such a threat can come in the form of the detonation of a neighboring warhead, fragment impact and direct shaped charge jet impact. In general, propellants formulated with binders that decompose endothermically are less sensitive than propellants formulated with binders that decompose exothermically, provided that these decomposition temperatures are not significantly higher than those of the energetic components. This endotherm in the thermoplastic gives the propellant the ability to absorb localized heat from hot fragments before the energetic materials can start to react significantly.

Although extensive work on the development of a LOVA propellant has been done over the past several years [4], and as a result some useful formulations have been found, considerable room for improvement still exists. The sensitivity of a candidate TPE cannot be adequately determined unless it is tested, and the results, whether or not this TPE appears promising, can still provide useful information on the development of future formulations.

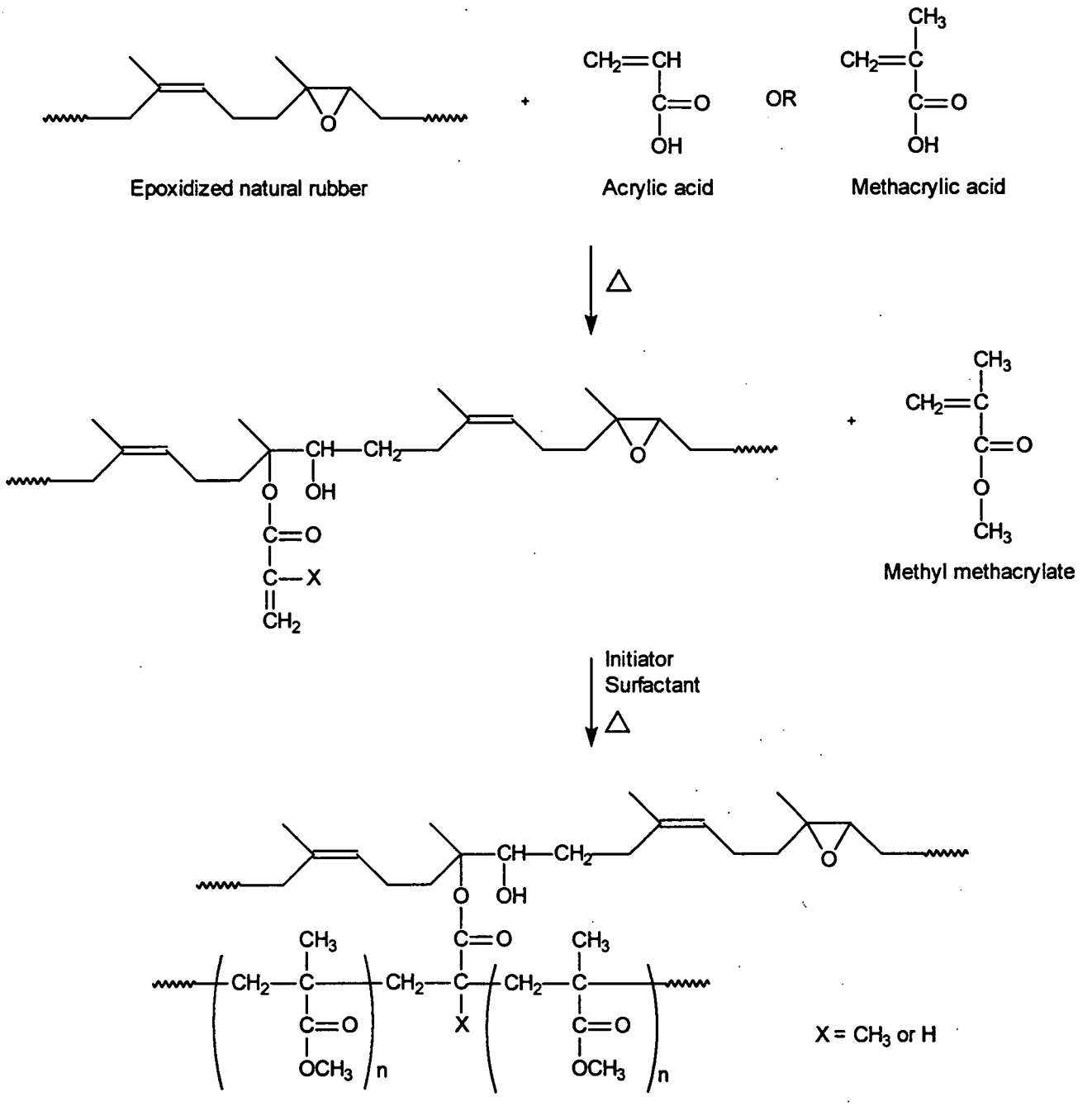


Figure 1: Chemical modification and grafting of epoxidized natural rubber.

2 OBJECTIVES

The objective here was to synthesize a LOVA binder by the grafting reaction of MMA with epoxidized natural rubber (see Figure 1).

To use extensive DMA / DEA analysis to:

- Study the chemistry of the grafting reaction.
- Prove phase separation.
- Check the degree of mixing from the T_g-values.
- Look at new properties of complex polymer systems, such as changes in the three T_gs, namely that of the starting materials, the mixed interphase and the phase separated polymerized monomer.
- Look at minor changes in T_gs that result from: the different techniques used for polymerization, changes in surfactant, changes in coupling technique to create the grafted material, different concentrations of starting material and external forces such as temperature annealing.
- Observe impact strength by the use of loss modulus. This is a novel technique.

3 EXPERIMENTAL

3.1 Materials

The materials used are summarized in Table 1. They were all supplied by Kumpulan Guthrie Berhad (Malaysia).

Table 1: Materials used in the synthesis of grafted ENR50.

Materials	Material Abbreviations
Epoxidized natural rubber (25 % mol epoxy groups)	ENR25
Epoxidized natural rubber (50 % mol epoxy groups)	ENR50
Thermoplastic epoxidized natural rubber	TPENR

The experimental set-up is shown in Figure 2 and a typical pre-emulsion polymerization formulation in Table 3.

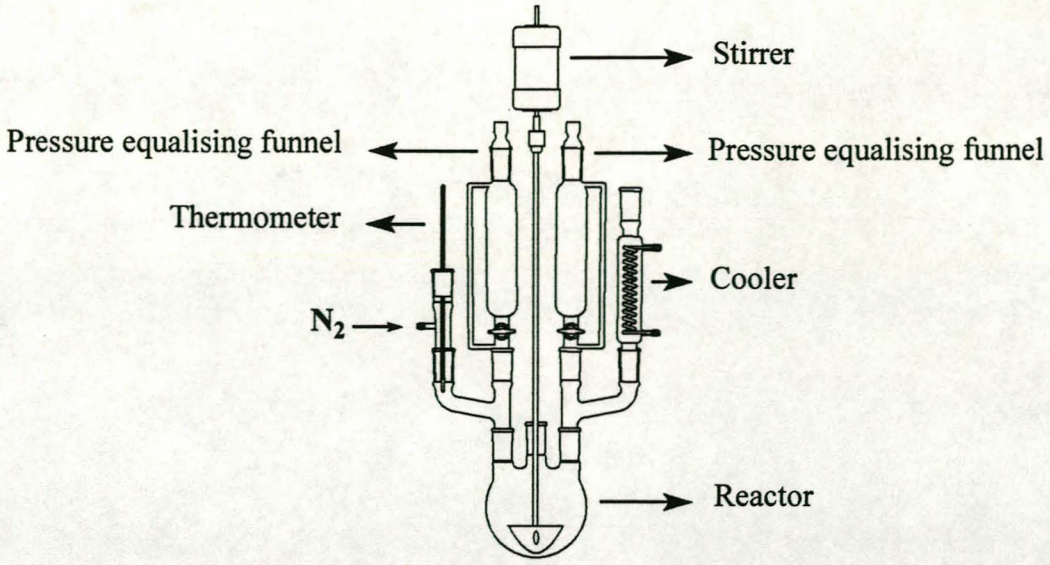


Figure 2: Experimental set-up used for the emulsion polymerization reaction of MMA with ENR50.

	Ingredients	Solids	%
	wt (g)	wt (g)	BOTM
Kettle charge			
DDI	14	-	-
Monomer Emulsion			
DDI	32.11	-	-
NP50 (Surfactant)	2.8	2.8	8
ENR50	31.81	17.5	50
MMA	17.15	17.15	49
AA or MAA	0.35	0.35	1
	84.71	37.8	
Initiator Solution			
DDI	7	-	-
Potassium Persulphate	0.7	0.7	2
	7.7	0.7	
	=====	=====	
	106.41	38.5	

Table 3: Formulation used for the reaction of ENR50 with MMA with the use of AA or MAA as a graft site.

3.2 Analysis of grafted ENR50 by DMA and DEA

Dynamic mechanical analysis (DMA) and dielectric analysis (DEA) are increasingly useful techniques for the characterization of polymers and viscoelastic properties. As polymers become increasingly popular and replace traditional materials in many applications, the information provided by these techniques is very useful to those in research and development, quality assurance and quality control, failure analysis and process control [5].

Dynamic mechanical analysis is the study of the movement of polymer chains by the application of a sinusoidally varying total force programmed in milliNewton (mN) onto the polymer [6]. The total force applied to the polymer is the sum of the static force and dynamic force with a chosen frequency in Hertz (Hz). The sample responds to the applied force with an oscillating amplitude, measured in micrometers (μm). The displacement amplitude corresponds to the average energy recovered in one cycle of oscillation in an elastic deformation. The sample also responds to the applied force with a phase lag (δ), reported in degrees (°). The phase lag corresponds to the average energy lost in one cycle of oscillation in a viscous deformation. Elastic and damping properties are calculated using fundamental relationships such as Hooke's law and Newton's law. From the amplitude the storage modulus (E'), and from the phase lag the loss modulus (E") is determined. The tan δ is the ratio of E" to E'. A schematic representation of the operation of DMA is shown in Figure 3.

Dielectric analysis is the study of the mobility of charged sites in a material [7]. These charged sites are typically ions or dipoles. The mobility of the dipoles and ions are measured by applying a sinusoidal voltage to the sample and measuring the current. Dipoles in the material will attempt to orient in the electrical field that is generated, while the ions will move to the electrode of opposite polarity. See figure 4. The measured current can be resolved into two fundamental dielectric characteristics: capacitance and conductance.

In dielectric measurements two items are very important: the A/D ratio and the base capacitance. The A/D ratio is the ratio of the electrode area (A) to the distance (D) between the electrode. In the experiments that were done the area of the top plate of the DMA is used, and the distance is the height of the sample. For accurate permittivity results it is also important to account for stray capacitance in the electrode configuration. This capacitance, known as the base capacitance, can be determined experimentally. As mentioned by comparing the applied voltage to the measured voltage two fundamental electrical characteristics can be determined, namely capacitance and conductance. This can be studied as a function of temperature, time and frequency and are used to determine other electrical properties [8].

A Perkin Elmer 7e Dynamic Mechanical Analyzer and an Eumetric System III Microdielectrometer were used simultaneously, to obtain dynamic mechanical and dielectric measurements. The parameters used are summarised in Table 4.

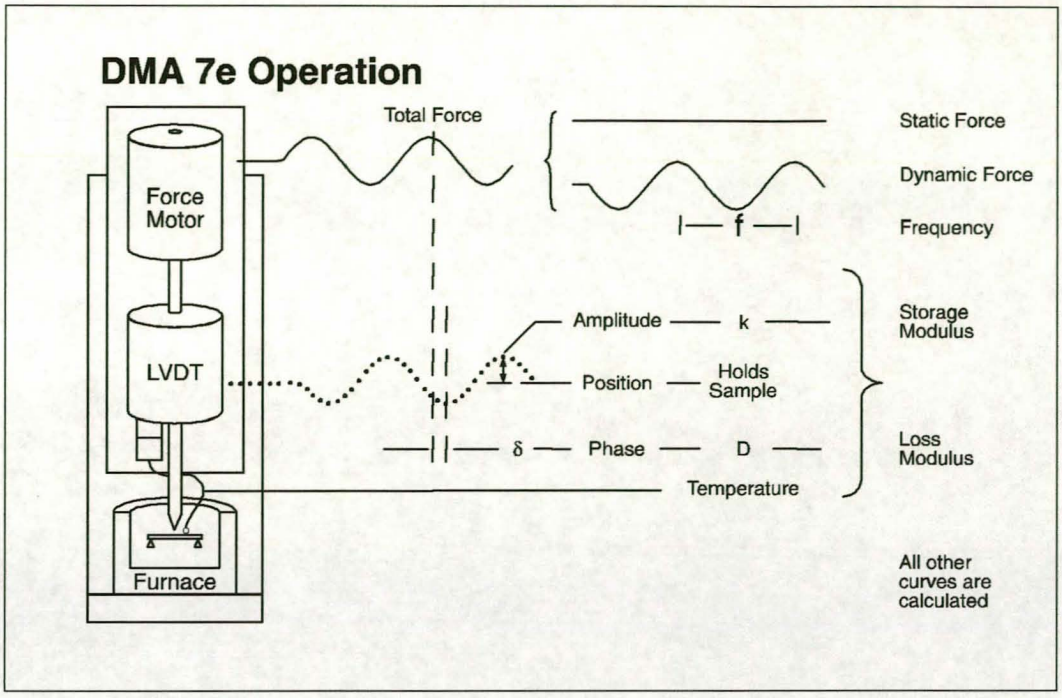


Figure 3: Schematic diagram of the operation of the DMA 7e.

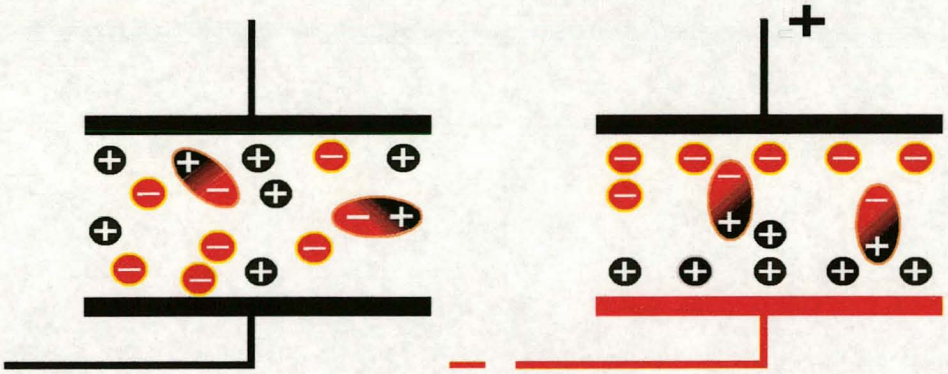


Figure 4: Representation of the orientation of dipoles and the movement of ions between the DEA electrodes [8].

Table 4: Parameters used in simultaneous DMA/DEA analyses.

Sample	Grafted ENR50	Disk
Instrumental	DMA	Perkin-Elmer DMA 7e with the DEA kit
	Measuring System	15 mm Cup and plate
	Geometry	Disk
Environmental	Purge	Nitrogen, (30 cc/min)
	Coolant	Liquid Nitrogen
Parameters	Mode	Temperature Scan
	Temperature Program	-60 to 160 °C at 5 C/min
	Static Force	Amplitude Control
	Dynamic Force	Amplitude Control
	Amplitude	8 µm
	Frequency	1.00 Hz
Instrumental	DEA	Micromet Eumetric System III Microdielecrometer
	Interface	Mid Conductivity
Parameters	Sensor	Mono/User
	A/D ratio	7.1 cm
	Base Capacitance	20 pF
	Frequencies	1, 10, 50, 100, 1000, 10000, 100000 Hz
	Cycle Time	15 seconds
	Duration	45 minutes

3.2 Analysis by GPEC

The most significant information regarding the grafted ENR50 can be obtained via non-exclusion chromatographic analyses, such as gradient polymer elution chromatography (GPEC) and liquid chromatography under critical conditions (LCCC). GPEC analyses on this material were done at the Laboratory of Polymer Chemistry at the Eindhoven University of Technology. Analyses were carried out to determine the amount of grafting of PMMA onto the ENR. GPEC also served to fractionate the various components of the material (ungrafted rubber, PMMA grafted rubber, free PMMA) in order to further analyze these specific components.

GPEC works on the following principle:
The sample is absorbed onto a chromatographic column. A gradient of non-solvent and solvent are then pushed through the column. At the highest non-solvent and lowest solvent levels the fraction with the lowest molecular weight will emerge first. As the solvent levels are slowly increased the higher molecular weight fractions, as well as the grafted material, will emerge from the column.

The set-up can be seen in Figure 5.

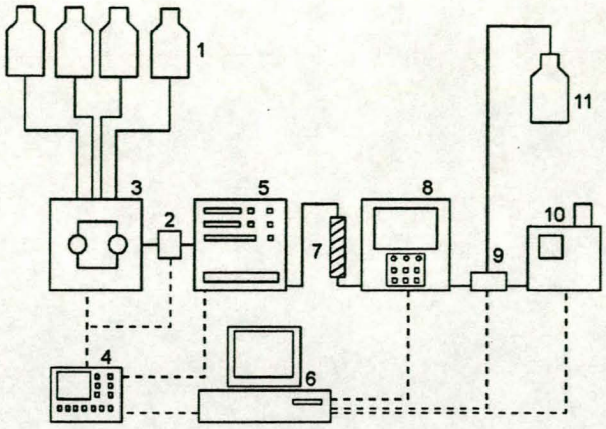


Figure 5: Schematic representation of a GPEC experimental set-up. Components are: (1) solvents, (2) mixing chamber, (3) gradient pump, (4) controller, (5) injector, (6) computer, (7) column, (8) UV detector, (9) switch valve, (10) ELSD detector, (11) solvent waste.

4 RESULTS AND DISCUSSION

4.1 Effect of method of polymerization on the T_g of the grafted material

Delayed addition of monomer and the pre-emulsion techniques were used successfully during the polymerization of MMA with ENR50. These techniques are suitable, from small to large quantities of MMA added, even where the ratio of ENR50 : MMA is 50 : 49 percent, based on the monomer weight. Results of polymerizations using these two techniques show some quite different results on the tan delta peak of the material formed during the reaction of ENR50 with MMA. The results of using these techniques on the T_g, where the formulation was kept the same, can be seen in Figure 6. The Perkin-Elmer DMA 7e dynamic mechanical analyser measured the tan delta vs. temperature curves and the T_g was taken as the onset of the tan delta peak.
Frequency was 1 Hz.

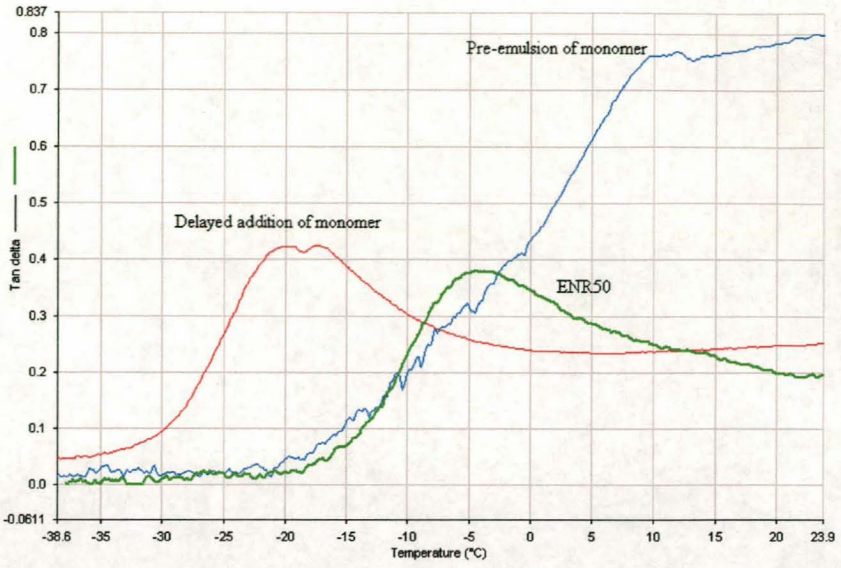


Figure 6: Tan delta vs. temperature curves to show the influence of the techniques used on the T_g.

The shift of the T_g of the rubber peak to lower temperatures proves that the rubber is selectively epoxidized i.e. it probably has a core in the latex particle with a lower degree of epoxidization. The reaction with MMA causes the low epoxidized rubber (with inherently lower T_g) to phase separate from the higher epoxidized rubber blend with the grafted PMMA.

4.2 Blending studies using homopolymer (ungrafted)

Blending studies with the different grades of ENR were done with 20%, 40% and 50% PMMA and with 20% PS.

The glass transition temperatures (T_g) of the blend ENR obtained from the tan delta vs. temperature plots are shown in Table 4. (The T_g was taken where the storage modulus curve started to drop.)

Table 4: Glass Transition Temperatures of the Polymer Systems and their homopolymers (at 1 Hz)

		T_g (°C)		
Polymer	Appearance	Homopolymer	1	2
ENR25	rubber	-20.8		
ENR50	rubber	-3		
TPENR	rubber	-18.3		
PMMA	plastic	104.8		
PS	plastic	110.9		
Blend				
ENR25/PMMA 20%	plastic		-34.6	106.5
ENR25/PS 20%	plastic		-35.7	111.7
Blend				
ENR50/PMMA 20%	plastic		-15.0	103.4
ENR50/PMMA 40%	plastic		-14.4	103.4
ENR50/PMMA 50%	rubber		-0.3	121.3
ENR50/PS 20%	plastic		-12.7	111.8
Blend				
TPENR/PMMA 20%	plastic		-12.2	96.0
TPENR/PS 20%	plastic		-5.5	99.1

4.3 Tan delta phase separation studies of the grafted ENR50 latex (comparing AA to MAA as graft site initiator)

Emulsion polymerization in the presence of seed latex show complex morphologies, including probably core-shell.

The tan δ vs. temperature plots for ENR50 grafted by MMA through graft site formation by AA and MAA are shown in Figures 7 and 8.

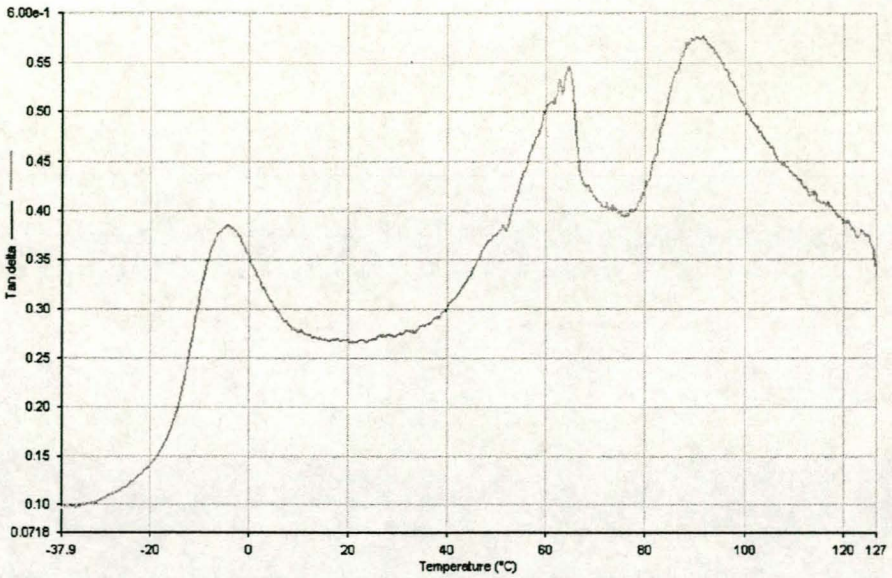


Figure 7: Tan δ vs. temperature curve for system A (ENR50/MMA/AA) at 1 Hz.

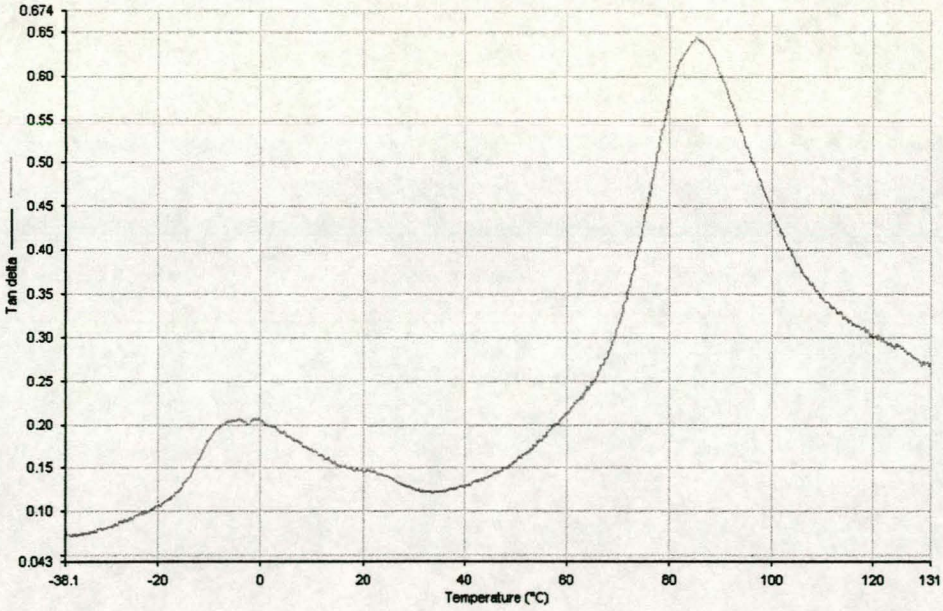


Figure 8: Tan δ vs. temperature curve for system B (ENR50/MMA/MAA) at 1 Hz.

The glass transition temperatures (T_g) are obtained from the E' and are shown in Table 5.

Table 5: Glass Transition Temperatures of polymer systems A and B and their hompolymers (at 1 HZ).

	T_g (°C)		
Polymer	Homopolymer	Ungrafted rubber	Grafted ENR50
ENR50	-5.1		
PMMA	106		
System A, ENR50/MMA/AA		-14.5	63.6
System B, ENR50/MMA/MAA		-13	49

The decrease in trough depth between the two tan δ transitions has also been used [9] as an index of mixing. Table 6 shows the results of this. System B (MAA) shows a higher tan δ value, indicating more mixing, while system A (AA) shows a relatively low value, indicating a lesser degree of mixing.

Table 6: The Intertransition tan δ values and the trough depth values for systems A and B.

System	Intertransition tan δ value	Trough depth
System A, ENR50/MMA/AA	0.27	0.31
System B, ENR50/MMA/MAA	0.14	0.50

4.4 Dynamic loss moduli

The dynamic loss modulus (E") vs. temperature plots for systems with A and B are shown in Figure 9 and 10. The polymer system A shows one poorly defined low temperature peak and one well-defined high temperature peak that is broadened appreciably into a shoulder by phase-separated PMMA. It will be shown later that in order to have a large impact resistance the lower temperature E" peak should be large. This is not the case in Figure 9, as it is in Figure 10.

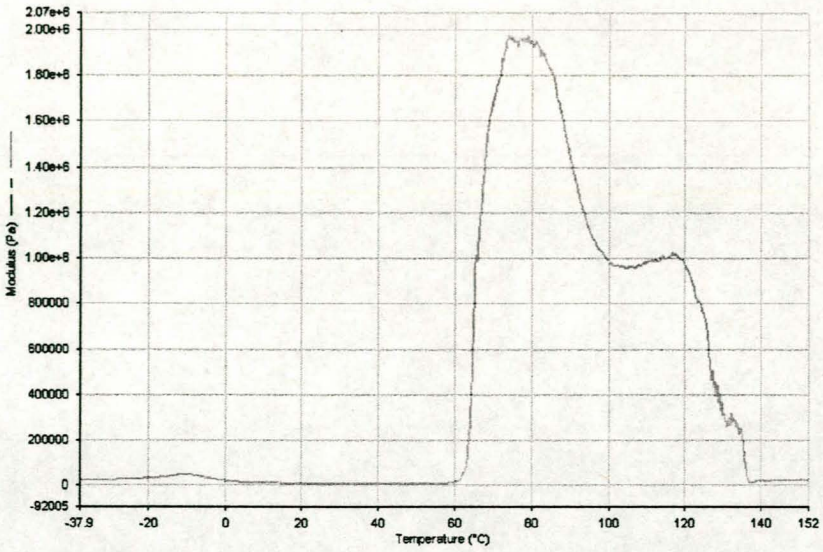


Figure 9: Loss modulus (E") vs. temperature curve for system A (ENR50/MMA/AA) at 1 Hz.

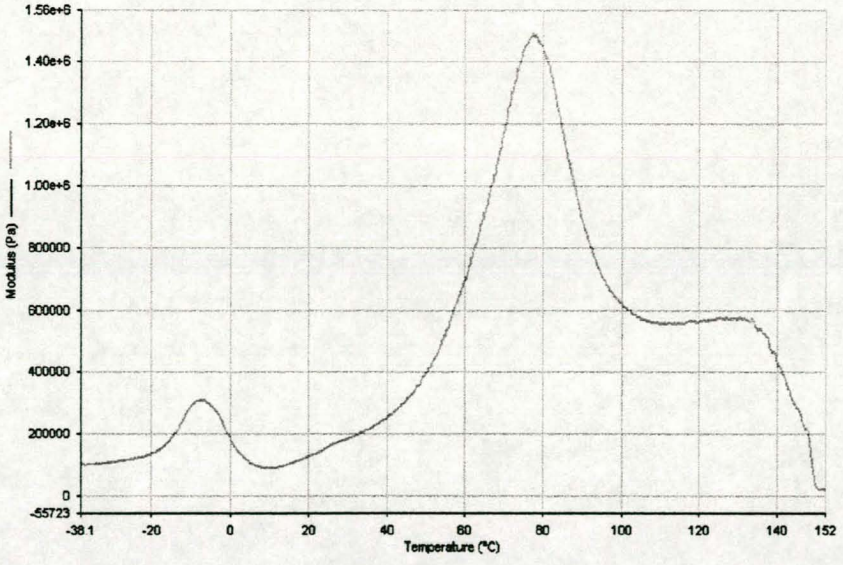


Figure 10: Loss modulus (E") vs. temperature curve for system B (ENR50/MMA/MAA) at 1 Hz.

4.5 Interrelation between DMA and DEA correlations

DMA and DEA grafts can be used to determine what parts of the peaks are due to polar and nonionic groups. See Figures 11 and 12.

The tan δ vs. temperature plot in figure 11 shows clearly the rubbery phase (ENR50), a grafted PMMA phase and a peak at 134.4 °C. The latter is the result of MAA that has homopolymerized in the emulsion. This may be due to inadequate mixing of the pre-emulsion. Phase separation is clearly in evidence due to the well-defined peaks. The tan δ vs. modulus plot in figure 11 also shows sharp drops, indicative of phase separation.

The log permittivity vs. temperature curve only indicates two peaks, respectively at 105 °C and at 134.4 °C. This is again the grafted PMMA and the PMAA peaks, the PMAA peak is very large compared to that of the DMA. This is due to the technique used. The DEA is very sensitive to dipoles and ions and therefore an acid such as PMAA will be prominent. The DEA does however not show any rubbery peaks. Because the DEA is sensitive to dipoles we can conclude that the epoxy group content has been reduced, probably in the small portion of the rubber that did not mix with the grafted material. In the original ENR50 the heterogeneous epoxidization of the latex particles appears to have left a less epoxidized core rubber particle that does not easily graft.

From these results it again appears as if the MAA has reacted with a few epoxide groups and that grafting has taken place from this site that was formed.

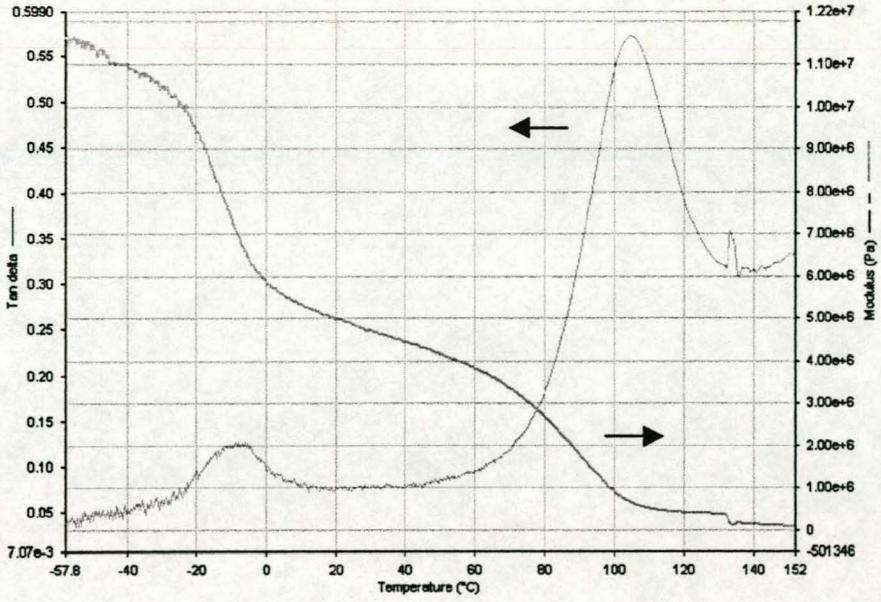


Figure 11: Tan δ and modulus vs. temperature plots for the reaction of ENR50 with MMA and MAA.

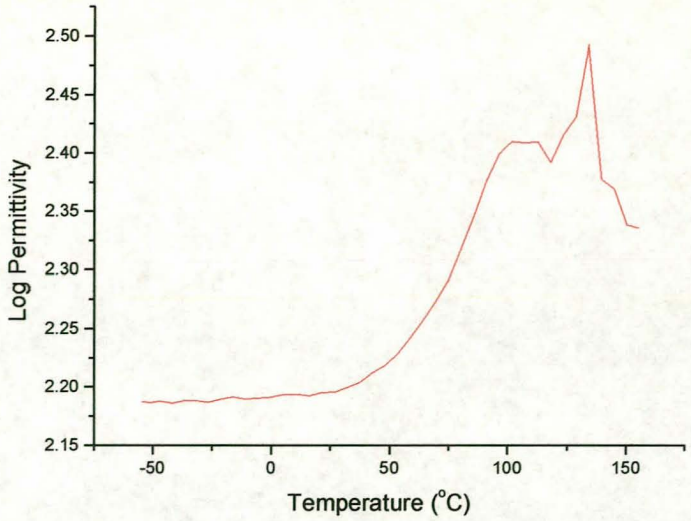


Figure 12: Log permittivity vs. temperature plot for system B (ENR50/MMA/MAA)

4.6 Corrobaration of grafting by an absorption / desorption reverse phase HPLC (GPEC)

The results of the grafted ENR50 can be seen in Figure 13.

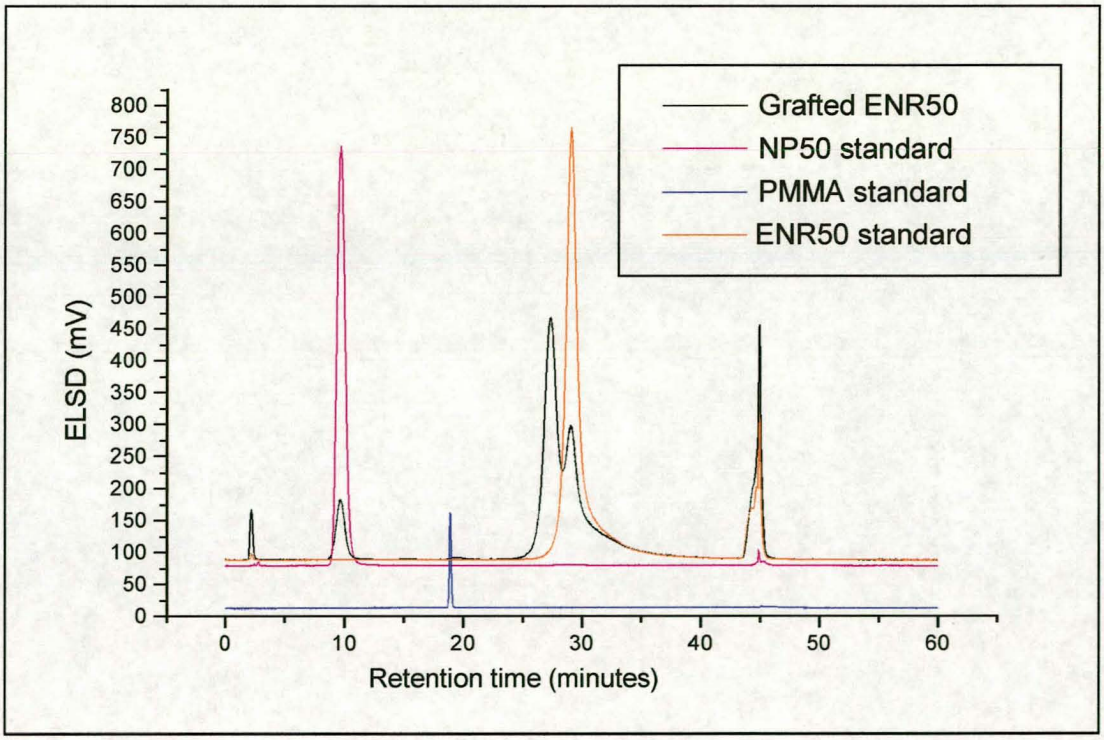


Figure 13: GPEC results of material formed during the reaction of MMA with ENR50.

The surfactant, as indicated by the NP50 standard, emerges first from the column at a retention time of 10 minutes. At a retention time of about 18 minutes, as indicated by the PMMA standard, we find no peak for homopolymerized methyl methacrylate. At a retention time of 30 minutes, as indicated by the ENR50 standard, the ENR50 emerges from the column. The peaks emerging after 40 minutes are the result of gel fractions. The remaining peak at 27 minutes is therefore the peak of grafted ENR50. We know now from these and the DMA-DEA results that we have unreacted rubber, grafted rubber and no homopolymer. The very clearly phase separated PMMA peak in the DMA spectra indicated phase separation in the grafted material.

4.7 Effects of different amounts of MMA on grafted ENR50

The results of using different amounts of MMA on grafted ENR50 are shown in figure 14.

From figure 14 it can be seen that the amount of MMA used has a significant influence on the T_g of the grafted material. As the amount of MMA is increased the T_g decreases (see Figure 15). This may be due to the non-random epoxidization of natural rubber [10]. The ENR therefore consist of highly epoxidized natural rubber blocks and less epoxidized natural rubbery blocks. As the MMA content is increased the separation of these blocks becomes more pronounced and the T_g tends to drop to the lower value of the less epoxidized natural rubber.

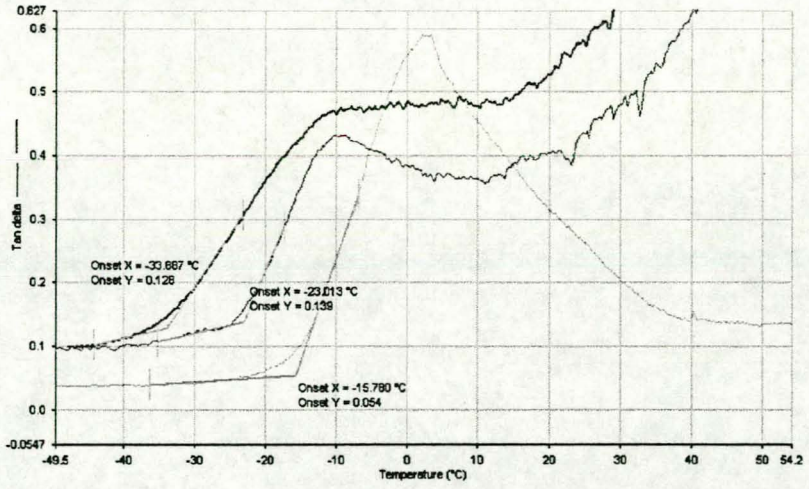


Figure 14: The effect of the amount of MMA in pre-emulsion polymerization on the T_g.

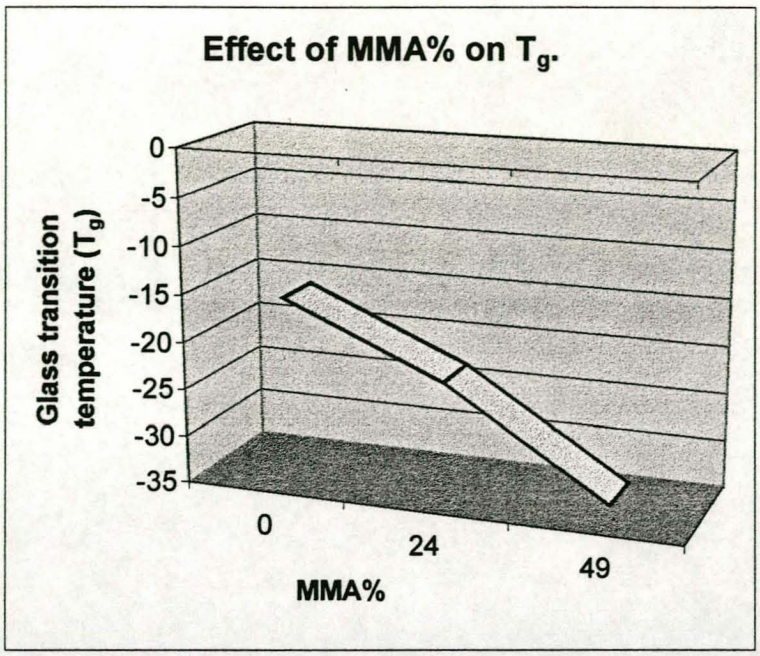


Figure 15: Effect of MMA% in pre-emulsion polymerization on T_g.

4.8 Impact resistance of the grafted epoxidized natural rubber

The major interest in two-phase systems e.g. grafted epoxidized natural rubber (ENR) with methyl methacrylate (MMA), centres on the ability of dispersed particles of a rubbery phase to improve the impact strength of a glassy matrix without corresponding plasticisation.

A novel method was used to characterize the impact performance of the grafted ENR50 that is independent of the total rubber content. This method was developed by H. E. Bair and B. Twombly [11]. They used it evaluate the impact performance of four acrylonitrile-butadiene-styrene (ABS) terpolymers. The results obtained correlated well with standard Izod impact tests [11].

Typical loss modulus curves for the grafted ENR50 formed during pre-emulsion polymerization of 49 % MMA with ENR50, are presented in Figures 16 and 17. Their results can be seen in Table 7.

Table 7: Evaluation of the area of the loss modulus peaks.

	Rubbery phase		Glassy Phase	
	AA	MAA	AA	MAA
Area of loss modulus peak (Pa x min)	1.04×10^5	6.68×10^5	7.72×10^6	5.84×10^6
Temp. of loss modulus peak (°C)	-10.3	-7.5	74.1	77.5

Here the rubbery and glassy phases correspond well according to the temperatures of the loss modulus peaks. There is a bigger difference between the area of the loss modulus peak of the rubbery phase than for the glassy phase. Seeing that, in the case of AA, the rubbery phase would be the restricting factor, it was decided to use MAA for further studies on the ENR50 because of the higher area and therefore the higher impact resistance.

4.9 Conclusion

It was shown conclusively, by GPEC, that grafting took place and this was also confirmed by DMA tan delta and loss moduli curves. Impact studies showed that MAA yield the best impact performance at low temperatures. The objective of creating a low and high temperature thermoplastic elastomer, that can be used as a propellant binder, with sufficient impact performance was therefore met. By using the right technique and the right amount of MMA these binder properties can be fine tuned for specific conditions.

In conclusion this paper shows that thermal mechanical and electrical techniques offer extensive characterization data, far in excess of normal calorimetric data, with which to study complex polymer phase structures.

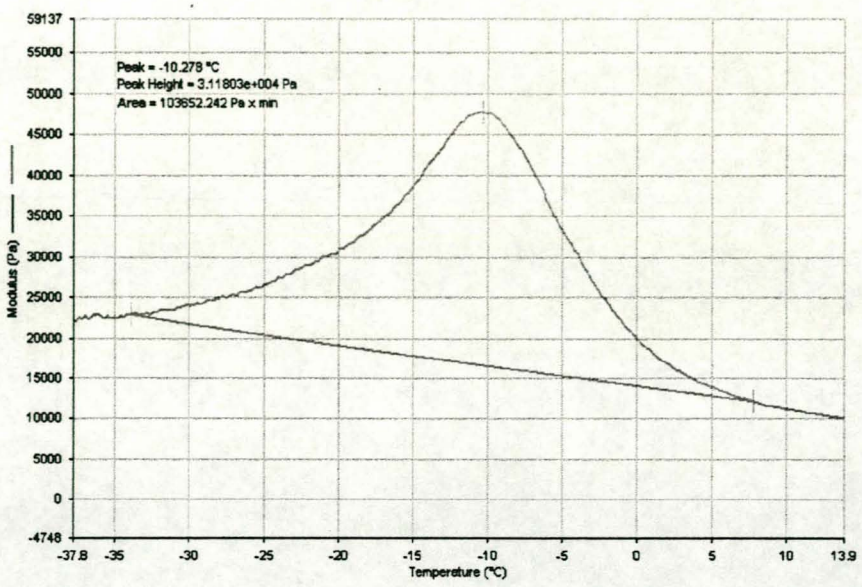


Figure 16: Typical loss modulus vs. temperature curve for rubbery phase where AA was used.

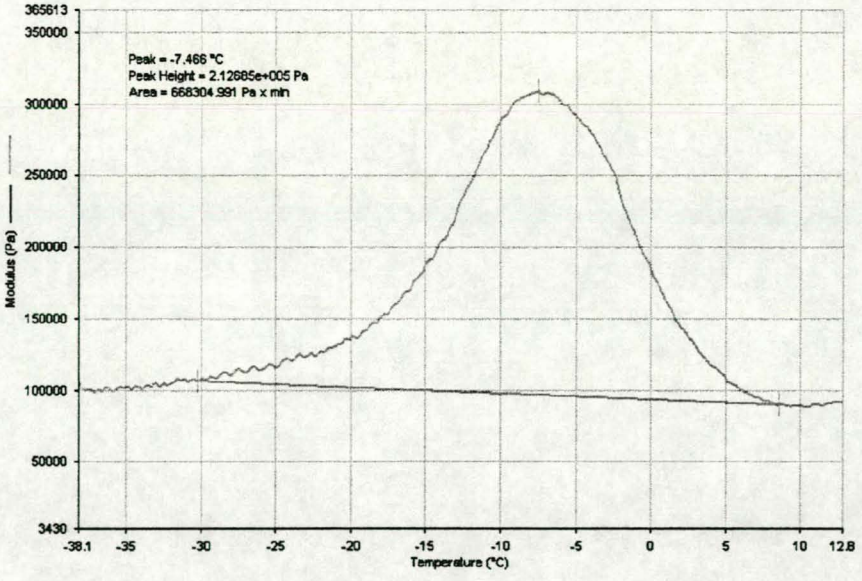


Figure 17: Typical loss modulus vs. temperature curve for rubbery phase where MAA was used.

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